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Polyurethane foam based packing media for biofilters removing volatile organic compounds from contaminated air

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POLYURETHANE FOAM BASED PACKING MEDIA FOR BIOFILTERS REMOVING VOLATILE ORGANIC COMPOUNDS FROM CONTAMINATED AIR

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ABSTRACT

In recent years, biofiltration technology has gained acceptance worldwide as an economical and reliable air pollution control technology for treating gases contaminated by low concentrations of biodegradable volatile organic compounds (VOCs). Important applications include control of odors generated by wastewater treatment plants and control of VOC emissions from industrial sources. Although there have been many successful applications, several operational problems have been reported in the literature. These include difficulty in control over bed moisture content, high head loss caused by excessive biomass production, and inability to maintain removal efficiency during transient periods of high concentration loading. Use of a superior packing medium may be able to mitigate these difficulties.

The research described herein was directed toward development and evaluation of novel biofilter packing media for use in aerobic biodegradation of VOCs present in contaminated air. Several types of media comprised of polyurethane foam and powdered activate (PAC) were manufactured and tested for suitability as biofilter packing media.

Experiments were conducted to determine the media's porosity, head loss, chemical resistance, and sorption capacity for several VOCs commonly present in industrial waste gases. Compounds tested included toluene, p-xylene, methyl ethyl ketone (MEK), and 4-methyl-2-pentanone (MIBK). These compounds are commonly used solvents that are found in the off-gases of many industrial processes including painting operations. Batch sorption experiments were conducted for equilibrium conditions (serum bottle studies), and fixed-bed studies were conducted for dynamic loading conditions (column studies). Appropriate mathematical models were applied to describe adsorption and desorption behavior of polyurethane foam for the VOCs tested. Bed depth service time analysis was used to predict the performance of the reactor under different experimental conditions.

Results reported herein indicate that polyurethane foam containing activated carbon contains the properties desirable for biofilter packing media. Such media are promising candidates for use in biofilters that are operated using sequencing batch operation.

CHAPTER 1 INTRODUCTION

In recent years, biofiltration technology has gained acceptance worldwide as an economical and reliable air pollution control technology for treating gases contaminated by low concentrations of biodegradable volatile organic compounds (VOCs). Although biofilters employing conventional organic packing media such as compost have been used successfully in many applications, there is currently a need for further research on ways to optimize the properties of biofilter packing media. Use of a superior filter bed medium could overcome or minimize many of the problems commonly encountered in biofilter operation (e.g., poor performance during transient periods of elevated contaminant loading, difficulty in control of moisture content, nutrient elimination, excessive head loss, and medium clogging).

In research described herein, several polyurethane foam based packing materials, some of which included powdered activated carbon (PAC), were manufactured and characterized to assess their suitability for use as biofilter packing media. Experiments were conducted to determine the media porosity, head loss, chemical resistance, and sorption capacity for several compounds commonly encountered in paint spray booth off-gases. Specific compounds tested were toluene, p-xylene, methyl ethyl ketone (MEK), and 4-methyl-2-pentanone (methyl isobutyl ketone, MIBK). Results demonstrate that PAC/polyurethane foam biofilter packing media can be designed and manufactured to contain substantially increased sorption capacity. A new operating strategy made possible with use of the PAC/polyurethane foam medium, sequencing batch operation, is proposed for treatment of mixtures of compounds commonly found in paint spray booth off-gases.

Research described herein was conducted to accomplish two primary objectives. First, to manufacture and characterize new biofilter-bed media that can overcome some of the problems encountered with conventional biofilter media, and second to develop a biofilter packing media that has the ability to accumulate undegraded contaminants within the time required for sequencing batch-operating strategies.

To achieve the objectives listed above the research was divided into several tasks, which are summarized below.

- Manufacture, Rinsing, and Initial Characterization of PAC/ foam Media

Thirteen types of polyurethane foam, twelve of which included powdered activate carbon (PAC), were manufactured using a method similar to that employed by Moe and Irvine (2000). The resulting foam cylinders were rinsed to remove excess surfactant and untrapped PAC. The final percent by mass of PAC in the foam cylinders was determined by accounting for the loss of PAC in the manufacturing and rinsing processes. Head loss, density, and batch sorption experiments (see below) were then conducted.

- Batch Sorption Experiments

Equilibrium isotherms for aqueous solutions of four different organic compounds (see Table 1.1) were determined at $23\pm1^{o}C$. Serum bottle experiments were conducted using all polyurethane foam /PAC formulations manufactured as well as commercially available polyurethane foam material which contained activated carbon. Equilibrium concentrations of aqueous samples were measured using liquid and gas chromatography. Freundlich isotherm parameters were used to model the sorption characteristics of the

various foams. Based on the results of the batch sorption experiments, two foam types were selected for further, more detailed, characterization.

Table 1.1: Properties of the studied compounds

Compound	Molecular Formula	CAS #	Molecular Weight (g/mole)	Density at 20°C (g/mL)	Solubility in water (mg/L)	Henry's Law Constant (atm*m^3/mole)
Toluene	C_7H_8	108-88-3	92.14	0.870	515	6.74E-03
p-Xylene	C_8H_{10}	106-42-3	106.17	0.866	185	6.90E-03
Methyl ethyl ketone (2-butanone)	C_4H_8O	78-93-3	72.11	0.805	22300	5.69E-05
Methyl isobutyl ketone (4-methyl-2-pentanone)	$C_6H_{12}O$	108-10-1	100.16	0.801	1900	1.38E-04

- Fixed-Bed Sorption and Desorption Experiments

Experiments to determine dynamic adsorption and desorption properties of the filter media were carried out using one o more glass columns with overall dimensions of approximately 125 cm in length and 9.9 cm diameter. Tested compounds were delivered by syringe pump through a glass syringe into an air stream where the compounds volatilized and them flowed through a packed bed containing polyurethane foam depths of up to 192 cm. Experiments ware conducted for a variety of influent gas flow rates and different concentrations for each compound tested.

- Modeling

The dynamics of adsorption for different combinations of individual VOCs and PAC/polyurethane foam media were modeled using a Bed-Depth Service Time (BDST) approach. The modeling effort was focused on translation of the empirical observations into a functional design relationship to predict the performance of columns subjected to sequencing batch operating strategies.

- Chemical resistance test

The two types of polyurethane foam selected for detailed characterization were tested for chemical resistance. Pre-weighed polyurethane foam samples were placed into amber glass bottles filled with different solutions and then sealed with teflon lined silicone septa caps. After 48 hours, The foam was visually inspected and the mass of foam in each bottle was weighed to determine if any variation occurred. Five different solutions were tested: toluene, methyl ethyl ketone, chlorine bleach, sodium hydroxide, and hydrochloric acid.

The organization of this thesis is as fallows. Chapter 2 of this thesis contains a literature review summarizing previous research and providing the rational for the research described herein. Chapter 3 describes the materials and methods used to manufacture foam and conduct the initial characterization the types of media tested. Results of the initial characterization are described in chapter 4. Chapter 5 describes the materials and methods used to conduct more detailed characterization of two types of foam selected for further study (based on results presented in chapter 4). Chapter 6 contains the results of the detailed characterization including the mathematical modeling

of the dynamic fixed bed sorption studies. Chapter 7 contains overall conclusions as well as recommendations for future research.

CHAPTER 2 LITERATURE REVIEW

2.1 Overview of Air Pollution Control

A wide variety of industrial process and environmental remediation activities generate gas stream contaminated by volatile organic compounds (VOCs). One example of this is off-gases generated during painting operations. Emissions of (VOCs) from painting operations are the largest source of manufacturing emissions for the automotive industry (Kim et al., 2000a, 2000b). Paint spray booth off-gases are also a concern for a number of other industry and government operations including military bases (McMinn et al., 1992). Smith and Brown (1993) estimated that nearly one million tons of solvents were emitted from paint spray booths nationally in 1987, with 409,100 tons consisting of hydrocarbons. The contaminant constituents present in paint spray booth off-gases vary depending on the type of paint utilized; however, a typical composition includes a mixture of solvents including acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl propyl ketone, toluene, benzene, and n-butyl acetate (McMinn et al., 1992; Webster et al., 1998; Kim et al., 2000a, 2000b; Kazenski and Kinney, 2000).

There are many effective air pollution control technologies, but not all can be applied to every waste stream (Deshusses, 1994). Selection of the technique appropriate for a particular application is guided by several considerations including the required removal efficiency, economic aspects, and regulatory requirements. The effectiveness of a technology depends on the particular application, but it can often be constrained by the gas flow rate and contaminant concentrations present.

The most widely used technologies for removing gas-phase pollutants from air streams, incineration and sorption to activated carbon, have substantial disadvantages. During incineration, pollutants are combusted at temperatures between 700 ^{o}C and 1400 ^{o}C. Although treatment performance is generally uniform with effective removal of most compounds, incinerators require large fuel input and may also produce harmful secondary waste streams including NOx. Carbon adsorption permits high removal efficiencies for low pollutant concentrations; however, this technology has high capital and operation costs because of the expenses of the medium and its disposal or regeneration. Furthermore, this process transfers contaminants from the gas to a solid phase that requires further treatment (Deshusses, 1994, and Devinny et al, 1999). An alternative to these technologies is biological treatment.

2.2 Biological Methods of Air Pollution Control

Biological purification of waste gas employs microorganisms to transform undesired components into innocuous products such as carbon dioxide, water, and biomass (Brauer, 1986). Biological off-gas treatment is based on the absorption of volatile contaminates in an aqueous phase or biofilm followed by microbial oxidation. It is appropriate for treating large flow rate air streams with low concentrations of biodegradable pollutants.

The major types of biological reactors for treatment of air-phase pollutants are biofilters, biotrickling filters, and bioscrubbers. The basic removal mechanisms are similar for all types; however, differences exist in the phase of the microbes, which

may be suspended or attached, and the state of the liquid, which may be flowing or stationary. Each of the major reactor types is summarized below.

Biofilters are not filtration units as strictly defined. Instead, they are systems that use a combination of basic processes: absorption, adsorption, desorption and degradation, of gas-phase contaminants. Microorganisms grow in a biofilm attached to the surface of a solid support medium. The filter-bed medium generally consists organic material (e.g., compost) or relatively inert substances (e.g., polyurethane foam cubes), both of which generally provide large surface attachment areas and some nutrient supply. Biofilters usually incorporate some form of water addition to control moisture content and add nutrients. In general, the gas stream is humidified before entering the biofilter reactor.

In biotrickling filters, microorganisms grow fixed to a rigid packing material or suspended in an aqueous phase. In contrast to biofilters, there is a free flowing liquid phase that flows over the packing media. As gas passes through the reactor, contaminants are transferred from the gas phase to a liquid phase, where they are subsequently biodegraded.

On the other hand, in bioscrubbers, contaminant absorption and contaminant degradation are carried out in separate reactors. Absorption may be achieved in packed columns, spray towers, or bubble columns. After initial contaminant absorption occurs, the liquid phase is transferred to a vessel where a fixed film or suspended consortium of microbes performs contaminant biodegradation. Biotrickling filters and bioscrubber systems have the disadvantage of requiring more complex construction and operation; however, they offer the advantage of increased operation control over pH, nutrient content, and other parameters (Devinny et al., 1999).

Leson and Winer (1991) concluded that biofiltration technology could provide significant economic advantages over other methods when applied to off-gases that contain readily biodegradable pollutants in low concentration**.** Ottengraf (1987) established that biofiltration can be a reliable and inexpensive technique appropriates for the prevention of air contamination in general.

2.3 Conventional Biofilter Design and Operation

A variety of materials have been used as biofilter support media including soil, wood chips, bark, sawdust, activate carbon, ceramic months, ceramic pellets, sintered glass, polystyrene beads, ground tires, polyurethane foam, polyurethane hydrogel, and some combinations of those (Baumgarten, 1987; DeFilippi et al., 1996; Bohn, 1996; Hodge, 1997; Kinney, 1998; and Moe and Irvine, 2000a and b). The organic and inorganic packing material characteristics depend on designer's objectives, and many different properties can be incorporated.

In addition to the primary support medium, a variety of additives may be used including bulking agents, buffers, nutrients, and microorganisms (Kinney et al., 1997). Whatever the packing material used, several desirable properties can be incorporated. These include high porosity, appropriate pore size, low density, and an ability to sorb water. One material that can be manufacture to contain all of these properties but which has not been extensively studied is polyurethane foam (DeFilippi et al., 1996; and Moe and Irvine, 2000a). Such a material may make possible application of a new operation strategy as described in section 2.5

2.4 Paint Spray Booth Off-gases

Although many constituents have been successfully treated using biological methods when they are present as individual compounds or simple mixtures, complex mixtures can be problematic when biological treatment processes are applied (Ottegraff et al., 1987). In treatment of mixtures of VOC contaminants, numerous researchers have reported that one or more compounds is not degraded until after other compounds have been degraded to very low concentrations. This frequently results in a spatial separation of zones for degradation of different compounds as a function of height in a biofilter bed. For example, during the operation of several laboratory-scale biofilters and biotrickling filters for treatment of a simulated paint spray booth waste stream, Kazenski and Kinney (2000) observed that degradation of toluene and p-xylene did not occur until after methyl n-propyl ketone, n-butyl acetate, and ethyl 3-othoxypropionate reached very low concentrations.

Similar results were reported by Webster et al. (1998) for contaminants commonly found in paint spray booth applications when treated in bench-scale and pilot-scale biotrickling filters. For a mixture of toluene, xylene, methyl ethyl ketone, and n-butyl acetate, although overall removal efficiencies were satisfactory (greater than 90%), removal of toluene was lower (approximately 70%) at a 39 second empty bed residence time (EBRT). Deshusses et al. (1999) reported that in treating a mixture of toluene and ethyl acetate, toluene removal was inhibited by presence of ethyl acetate. Additionally, Deshusses et al. (1995) observed that methyl isobutyl ketone degradation rates were adversely affected by presence of methyl ethyl ketone. Such effects, particularly for mixtures of ketones, have been known for quite some time. For instance, Mahmoud and Davis (1970) reported that in batch experiments with suspended growth cultures, acetone was not removed until concentrations of methyl ethyl ketone and methyl propyl ketone reached low levels even though acetone removal was immediate for samples where it was the sole compound. Similarly, Irvine et al. (1973) reported inhibition of acetone degradation in the presence of methyl ethyl ketone and diethyl ketone in batch activated sludge cultures.

Although problems associated with inhibition or other complex kinetics can be overcome by designing biofilters with sufficiently deep beds or sufficiently long residence times to allow for complete degradation of different compounds at different locations in the bed, such solutions can be problematic for the unsteady-state conditions frequently encountered in industrial painting operations. This effect can be readily observed in data reported by Deshusses et al. (1999) for a mixture of ethyl acetate and toluene. Presence of ethyl acetate was found to inhibit degradation of toluene. Consequently, toluene degradation occurred only in sections of the biofilter column furthest from the inlet where ethyl acetate concentrations were low. When the inlet ethyl acetate concentration was sufficiently high that it was present throughout the entire height of the biofilter column, toluene passed through the column almost completely undegraded in spite of the presence of toluene-degrading microorganisms. For paint spray booth off-gases, during transient periods of elevated contaminant loading (i.e., a “shock load”) when the contaminant loading rate exceeds the biological reaction capacity for the most readily degraded compounds, essentially no degradation of less readily degraded compounds can occur. Such results are especially problematic

when the less readily degraded compounds (e.g., benzene) pose larger health risks than the more readily degraded compounds.

2.5 Periodic Treatment Systems

A potential solution to the problem of inhibition (and concomitant sequential degradation) is use of periodic biofilter operating strategies, specifically, sequencing batch operation. A sequencing batch operated biofilter system would normally include two or more reactors. Terminology established for each portion of the cycle of a periodically operated biofilter system is as follows (Irvine and Moe, 2001a):

- FEED: period during which contaminated gas flows to one of the reactors or to a grouping of the reactors in a multiple biofilter system. Contaminant removal during FEED results from some combination of sorption and biological transformation. At the end of FEED, REACT begins as the inflow of contaminated gas is diverted to the next reactor or grouping of reactors in the system.
- REACT: period during which contaminants are biotransformed to acceptable products. Air may or may not be recirculated within the reactor or grouping of reactors. Addition and/or recirculation with uncontaminated air or pure oxygen may be necessary if oxygen is the desired electron acceptor.
- IDLE: period between FEED and REACT during which the reactor or grouping of reactors awaits the beginning a new cycle. Oxygen may or may not be added during IDLE. If added, uncontaminated air may be recirculated or passed continuously through the biofilter. The biofilter's excess capacity is measured by the total time in IDLE because the time could be easily re-allocated to REACT (or FEED) if necessary.

In practice, periodicity can be achieved using a variety of biofilter configurations and loading strategies for both normal and uncontrolled transient loading conditions. One such configuration, previously described by Martinez et al. (2000), designed to operate in sequence is shown in Figure 2.1. As depicted in the figure, the black filter bed shown in the FEED period represents a biofilter with accumulated substrate. The gray biofilter bed shown in the REACT period represents a biofilter with some stored substrate but in a quantity less than the peak amount accumulated during FEED. The white biofilter bed shown in the IDLE period represents a biofilter with no stored substrate. In applications where there is an intermittent discharge of contaminated gases (e.g., during an eight hour work day), it may be possible to use a single biofilter, while in cases where a continuous contaminated gas flow is generated, multiple units installed in parallel and operated in sequence will be necessary (Irvine and Moe, 2000a).

Contaminant accumulation requires that there be an appreciable reduction in the empty bed residence time (EBRT) and that the microbes selected and/or the medium used for the packing material be able to "sorb" the contaminants without completing the biotransformation process during FEED. The task of biotransformation completion would take place during REACT with "famine" conditions continuing after the biodegradable contaminants are fully transformed. Because biodegradation would occur in a batch-mode during REACT, it may be possible to overcome kinetic limitation caused by inhibition and repression encountered in continuous flow systems provided that REACT is sufficiently long to allow for degradation of the most slowly

degraded constituent. Similar operating strategies have been used with success for treating wastewaters containing inhibitory compounds (see for example Chozick and Irvine, 1991). In addition, several studies in recent years indicate that periodic loading strategies can improve biofilter treatment performance during unsteady-state transient loading (Song and Kinney, 2000; Irvine and Moe, 2001; Moe and Irvine, 2001).

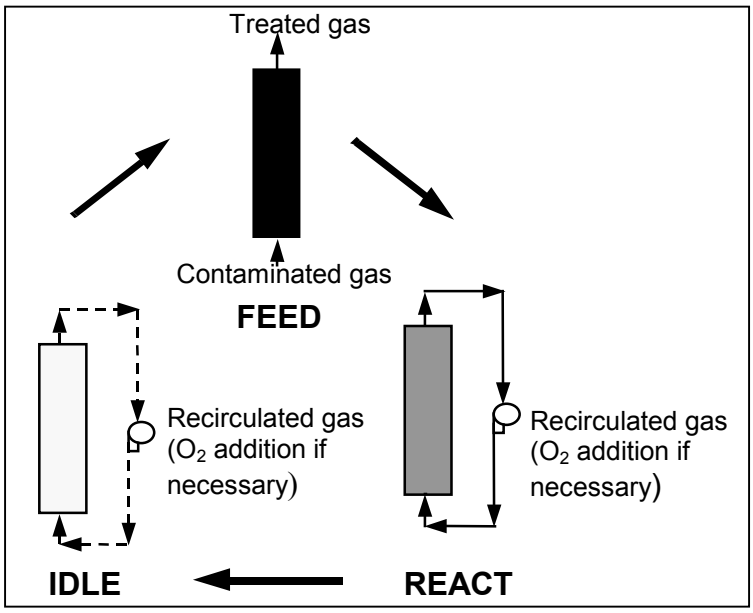

Figure 2.1: Cycle for one biofilter in a periodically operated multiple-tank biofilter system

2.6 Polyurethane Foam Support Materials

A medium that may contain the properties necessary for successful sequencing batch operation in biofilter systems is polyurethane foam containing powdered activated carbon (PAC).

Because the choice of starting molecules is great, the properties of polyurethane foam media are wide. Choice of the polyol has a major effect on foam properties, especially rigidity and flexibility (Braun et al., 1985). Foam density, cell structure, rate of wetting, and water retention can be modified to develop a wide range of foam characteristics by controlling the ratio of water to prepolymer, foaming temperature, pH, and the type and amount of surfactant (Havens and Rase, 1993). By adding varying amounts of PAC or other sorbents to the foam mixture, the sorption characteristics may be altered. Moe and Irvine (2000a) found that homogenous polyurethane foam could be made in the laboratory with low head loss, high porosity, high surface area, and an ability to readily sorb water and nutrient solutions. Such media permit use of novel nutrient addition and biosolids wasting strategies in biofilters treating contaminated gases (Moe and Irvine, 2000b).

Although these previous studies indicate that polyurethane foam may offer advantages over conventional packing media, relatively little is known about the properties of polyurethane foam manufactured to include activated carbon to increase

the sorption capacity. In the studies described herein, several types of polyurethane foam media were manufactured using different concentrations of PAC as an integrated part of the foam in an attempt to create packing media with a wide range of sorption characteristics. The media were analyzed to determine their suitability as a solid support medium for use in batch-operated gas-phase biofilters. Additionally, commercially available polyurethane foam coated with activated carbon was also evaluated.

2.7 Powder Activated Carbon (PAC)

The process of contaminant adsorption to activated carbon, in a system containing free water is generally thought to involve three steps: macrotransport, microtransport, and sorption. Macrotransport involves movement of an organic compound through water to the liquid-solid interface by advention and diffusion. Microtransport involves diffusion of the organic compound through the macropore system of GAC to adsorption sites in the micropores and submicropores of GAC. The term sorption is used because it is difficult to differentiate between chemical and physical adsorption. Sorption results in the accumulation of a chemical species on the interface between the two distinct phases. Solute adsorption from liquid solution on a solid surface can be thought of the net result of the competition between the surface and the solvent for solute molecules (Metcalf and Eddy, 1991).

Adsorption process using granular activated carbon (GAC) or powdered activated carbon (PAC) have been used extensively as the final stage in water, ground water, and wastewater treatment to remove trace levels of hazardous organic contaminants (Faust and Aly, 1987; Noll et al., 1992; Kold and Wilderer, 1995 and 1997). Numerous process configurations have been used with activated carbon in the form of GAC or PAC and with the carbon fixed (i.e., packed bed) or moving (e.g., fluidized bed or suspended). Various examples include the adsorption of organic compounds such as PAHs and BTEX by fluidized bed activated carbon absorbers as studied by Chiang and coworkers (2000). Campos et al. (2000) investigated the application of powdered activated carbon (PAC) to an upflow floc blanket reactor used to reduce the concentration of organic compounds present in drinking water sources. Othman et al (2001) studied removal of dissolved organic compounds in fixed-bed columns containing various activated carbons made from Victorian low-rank coal and commercial adsorbents under continuous flow conditions. Bed depth service time analysis (see section 2.8) was used to predict the performance of columns. Whatever the process configuration utilized, activated carbon is relatively expensive, and its limited adsorption capacity makes periodic replacement or regeneration necessary.

As an alternative to conventional methods for regenerating activated carbon (e.g., using steam), GAC adsorption is increasingly being integrated with degradation processes into hybrid systems that utilize biological pollutant removal and activated carbon regeneration in the same unit. Suidan and coworkers (1986) studied the degradation of phenol using a packed bed containing microorganisms attached to a GAC. Chozick and Irvine (1991) studied integration of GAC into a SBR for treatment of VOC contaminated waters using a process known as the granular activated carbon-sequencing batch biofilm reactor (GAC-SBR). Kold and Wilderer (1995) developed

two types of activated carbon membrane biofilm reactors for degradation of volatile organic pollutants. They combined membrane aeration technology and activated carbon adsorption with biological treatment in order to biologically degrade VOCs in industrial wastewater. In further studies, Kold and Wilderer (1997) tested a GAC-SBR to treat industrial wastewater. They found that a combination of activated carbon and biodegradation technology produced additional advantages.

Paca and Koutsky (2000) studied the effect of granulated activated carbon on styrene removal in a gas-phase biofilter. They compared two different packing materials (Perlite and GAC) on performance characteristics, and concluded that using GAC resulted in a much higher elimination capacity than was achieved using Perlite, a material with little adsorption capacity.

Use of activated carbon as part of a solid porous foam matrix to support attached microbial growth in bioreactors for organic pollutant removal has been reported by some authors. Lupton and Zupancic (1991) utilized a porous biomass support system that used open-cell foam within which was entrapped small particles of activated carbon and suitable microorganisms. This invention was directed toward aerobic biodegradation of organic pollutants in aqueous media with particular emphasis on phenolic compounds as organic pollutants. A similar approach was reported by Lupton et al., (1995) who relayed a process for reducing the concentration of organic pollutants such as phenol in waste water stream by passing the stream through a bioreactor containing flexible hydrophobic polyurethane foam impregnated with activated carbon and aerobic microorganisms capable of metabolizing the organic materials.

DeFilippi et al., (1996) presented an invention that provides a process for remediation of vaporous pollutants which comprises passing a vaporous stream containing one or more pollutants through a bioreactor. The bioreactor comprising a plurality of biologically active packed bed that was comprised, in part of a macroporous substrate, which was fabricated from polyurethane and coated with activated carbon.

2.8 Simulation and Design Model for Adsorption Processes

Various mathematical models have been developed to describe contaminant sorption to activated carbon in many of the diverse applications for which it is used. Mathematical models can facilitate the design and analysis of full-scale systems by reducing the number of pilot-scale test required to evaluate various operating conditions and design parameters for sorption. Weber and smith (1987) expressed that models can generally be calibrated from simple and well-controlled bench-scale experiments thus positioning pilot test programs principally for verifications of the design bases rather than for primary data development.

The main obstacle in using mathematical models for design and analysis of sorption system is that they typically require many input parameters, some of which may be site-specific and can be obtained only experimentally. Furthermore, sufficient knowledge of various adsorption model options is required for a designer to select an appropriate adsorption model and the sequence of the model applications to predict the adsorber performance in removing VOCs (Hand et al., 1997.)

Several researchers have attempted to predict contaminant removal by sorption. Bulloch et al, (1998) developed a model to predict multicomponent adsorption equilibrium behavior using single-component isotherm parameters and fictitious components representing the background matrix. Traegner and Suidan (1989) performed batch experiments to determine the mass transfer as well as adsorption equilibrium parameters to solve the mathematical homogeneous surface diffusion model (HSDM). Dipak et al. (1993) studied a new method of solving the homogeneous surface diffusion model for activated carbon adsorption, which reduces the complexity of the solution methodology for HSDM, to develop solutions that are continuous in time.

Furayu et al. (1996) used a column of activated carbon to develop a mechanistic design model for the adsorption of phenols. Also, Choy et al. (2000) studied the Langumuir isotherm model applied to the multicomponent sorption onto activated carbon. Chatzopoulos and Varma (1995) described a model for aqueous-phase adsorption and desorption of toluene in activated carbon fixed beds.

In general, there are two different types of models that can be applied to describe the sorption properties of activated carbon or other carbonaceous adsorbents: 1) equilibrium isotherm models, and 2) dynamic models.

The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and temperature. Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called an adsorption isotherm. Numerous empirical equations have been developed to model experimental isotherm data. Frequently used isotherm models include the Freundlich isotherm, Langmuir isotherm, and Brunauer, Emmet, and Teller (BET) isotherms. Of these three, the Freundlich isotherm is used most commonly to describe the adsorption characteristics of activated carbon (Metcalf and Eddy, 1991)

The empirically derived Freundlich isotherm equation is defined as:

$$\frac{x}{m} = k_f C_e^{1/n} \qquad (2.1)$$

Where:

$\frac{x}{m}$ = amount adsorbate adsorbed per unit weight of adsorbent

Ce = equilibrium concentration of adsorbate in solution after adsorption.

K_f and n = empirical constants

Adsorption isotherm experiments and models provide useful information regarding the mass of contaminant sorbed to activated carbon under equilibrium conditions; however, sorption systems in full-scale systems are often at non-equilibrium conditions. Bohart and Adams developed a dynamic relationship based on a surface-reaction-rate theory, which can be used to predict the performance of continuous-flow activated carbon columns. Hutchins presented a modification of the Bohart-Adams equation which requires only three column tests to collect the data necessary for model calibration. This is called the Bed-Depth Service Time (BDST) approach. The Bohart-Adams equation can be expressed as:

$$t = aX + b \qquad (2.2)$$

where X = depth in column

$$a = \frac{N}{C_{in} \times V} \qquad (2.3)$$

where:

a = slope (h/m)

N = adsorptive capacity of packing media (mass of contaminant removed per volume of packing media in the column kg/m^3)

C_{in} = influent contaminant concentration (mg/L)

V = superficial velocity through column (m/h) (m^3/h per m^2 of column)

$$b = \left(\frac{1}{K \times C_{in}}\right) \times \ln\left[\left(\frac{C_{in}}{C_{out}}\right) - 1\right] \qquad (2.4)$$

where:

b = intercept (h)

K = adsorption rate constant required to move an adsorption zone through the critical depth (m^3/(kg h)) (m^3 of gas treated per kg impurity fed per hour)

C_{out} = contaminant concentration at breakthrough (mg/L)

If a value of a is determine for one flow rate, values for other rates can be computed by multiplying the original slope by the ratio of the original and new flow rate. The b value change is not significant with respect to changing flow rates. Adjustment for changing initial concentration can be made as follows:

$$a_2 = a_1 \frac{Q_1}{Q_2} \qquad (2.5)$$

$$b_2 = b_1 \frac{C_1}{C_2} \frac{\ln(C_2 / C_f - 1)}{\ln(C_1 / C_b - 1)} \qquad (2.6)$$

In order to develop a BDST correlation, a number of pilot columns of equal depth are operated in series and breakthrough curves are plotted for each. These data are then used to plot a BDST correlation by recording the operating time required to reach a certain removal at each EBCT. The slope of the BDST line is equal to the reciprocal of the velocity of the adsorption zone and the X intercept is the critical depth defined as the minimum bed depth required to obtain the desired effluent quality at time zero. If the adsorption zone is arbitrarily defined as the media layer through which the gas or liquid concentration varies from 90 to 10 percent of the feed concentration, then this zone is defined by the horizontal distance between these two lines in the BDST plot (Eckenfelder, 2000).

CHAPTER 3 MATERIALS AND METHOD FOR PRELIMINARY EVALUATION

3.1 Medium Production and Preparation

Several types of packing media were characterized to assess their potential for use in biofilters. Fourteen types of polyurethane foam, thirteen of which included powdered activate carbon (PAC), were manufactured for use in the experiments described herein. The following sections explain the procedures used to manufacture and rinse the polyurethane foam media that were tested. One additional packing medium, consisting of polyurethane foam cubes with an activated carbon surface coating, was obtained from a commercially available source. The latter packing medium is described in section 3.1.4.

3.1.1 Pulverizing and sieving activate carbon

Two types activated carbon were tested in different foam formulations. Both types were prepared by pulverizing granular activated carbon (type F-300 from Calgon Carbon Corporation, Pittsburgh, PA, and type SN from Westvaco, Charleston, SC) using a Hamilton Beach laboratory blender (Washington, NC) to obtain powdered activate carbon (PAC). The resulting PAC was then separated into different size fraction using a sieve shaker (W.S. Tyler Company, Cleveland, OH). PAC particles which passed through a No. 200 series standard sieve (74 μm nominal opening) were then collected and dried in an oven at 105 ^{o}C for at least 24 hours before use in foam manufacture.

Table 3.1: Surfactant properties

Surfactant Type	Molecular Formula	Molecular Weight (g/mol)	Critical Micelle Concentration (mol/L)
Pluronic^{TM} P-65	$HO\text{-}(CH_2CH_2O)_X\text{-}(CH_2CHO)_Y\text{-}CH_3\text{-}(CH_2CH_2O)_X\text{-}H$	3400	* N.A.
Sodium dedocyl sulfate	$CH_3(CH_2)_{11}OS_3Na$	288.4	8.6×10^{-3}
Tween® 80	$C_{64}H_{124}O_{26}$	1309.7	1.26×10^{-5}

* Not applicable because Pluronic P-65 does not form micelles

3.1.2 Foam Manufacture

The general procedure to manufacture polyurethane foam was to mix equal masses of a polyether prepolymer that contained a cross-linking agent with an aqueous surfactant solution. Foaming occurs upon reaction of the prepolymer with water, and the resulting foam was allowed to grow and solidify after it was placed in a cylindrical cardboard mold. The pore structure of polyurethane foams can be altered by the

addition of surfactants. Activated carbon was incorporated in the foam media by adding pre-weighed amount of PAC into surfactant solution before it was mixed with prepolymer. Specific information regarding the of each foam formulation is described below.

Three different surfactants were used at various concentrations in the different foam formulations. Surfactants tested were Pluronics^{TM} P-65 (BASF Corporation, Mount Olive, NY), Sodium dedocyl sulfate (SDS) from Aldrich Chemicals (Milwaukee, WI), and Tween® 80 from Aldrich Chemicals (Milwaukee, WI). Properties of those surfactants are summarized in the Table 3.1.

In the procedure used to make foam with the first surfactant, Pluronics^{TM} P-65, surfactant solution was made by dissolving 30 g Pluronics^{TM} P-65 surfactant in 1.0 L of deionized water, and then cooling to 8^{o}C in a laboratory refrigerator. Hypol^{TM} 3000 prepolymer (Hampshire Chemical Company, Lexington, MA) was heated to 55^{o}C in constant temperature water and maintained at that temperature for at least 2 hours before use. The manufacturing process consisted of adding a pre-weighed amount of PAC to 120 g of surfactant solution, and mixing with a high torque mechanical mixer (Lightning, Rochester, NY) at a speed of 1000 rpm. The surfactant solution/PAC mixture was poured into a cup containing 120 g Hypol^{TM} and mixed using a high torque mechanical mixer at 1000 rpm for approximately 20 seconds. The Hypol/Surfactant Solution/PAC mixture was then poured into a cylindrical cardboard mold 10.5 cm in diameter and 23 cm tall. The foam was allowed to cure in a fume hood at least for one hour before the mold was removed. The manufacturing process was repeated several times using different masses of PAC. Specific formulations made using this process, arbitrarily named Formulations A to E, are summarized in Table 3.2

For foam formulations arbitrarily named F to K as well formulation M, the manufacture procedure was essentially the same as previously described; however, there were two notable exceptions. First, the surfactant type and concentration were different as noted in table 3.2. Second, PAC was mixed initially with 60 g of deionized water, and later mixed with 60 g of surfactant solution prior to mixing with prepolymer. The surfactant concentration listed in table 3.2 is that after the PAC/water was mixed with surfactant solution, (e.g., for Formulation F, 60 g of DI water was mixed with PAC and then 60 g of solution containing 20 g/L SDS was added to give a final surfactant concentration of 10 g/L prior to mixing with prepolymer).

A third process was used for foam formulations L1 and L2. For these formulations, toluene was sorbed to Westvaco type SN PAC prior to its use in foam manufacture. Details regarding the PAC preparation process can be found in Appendix 2. For Foam formulation L1, 60 g of deionized water was added to each beaker counting toluene sorbed PAC, and the contents were manually mixed using a plastic stirrer to form a slurry. Then, 60 g of Tween 80 surfactant solution was added to the slurry, and it was mechanically mixed at 1000 rpm. The final resulting mixture was poured into a cup containing 120 g of Hypol 2000 heated to 55 ^{o}C as previously described. The rest of foam manufacture process was the same as that previously described. Foam Formulation L2 was made exactly as foam Formulation L1 except

that, instead of 60 g of deionized water add to each beaker for foam Formulation L1, 120 g was added for this new formulation.

3.1.3 Foam rinsing procedure

After foam was allowed to cure for at least one hour, the cardboard molds were removed, and the top and the bottom 1 cm of each cylinder were sliced off using a disposable microtome blade. Resulting foam cylinders were dried in a laboratory oven at 65 ^{o}C for 24 hours before they were weighed and then rinsed to remove excess surfactant using the following procedure. The dry foam cylinders were wetted with deionized water until they were 70% moisture content (m/m). The wet cylinders were then placed in a plastic bucket containing 1.8 L of deionized water per foam cylinder. The cylinders were squeezed after they were submerged in water to dislodge air bubbles. After soaking in water for at least three hours, each cylinder was removed from the bucket and manually compressed to remove excess water and adjust to 70% moisture content, and then submerged in new deionized water. This process was repeated until there was less than 0.5 mg/L (as soluble TOC) of surfactant remaining in the foam rinse water. Finally, the foam cylinders were dried in a laboratory oven at 65^{o}C for several days before use in subsequent experiments.

An additional rinsing procedure was applied to foam formulations J and M. After surfactant remaining in the foam rinse water (using the previously described procedure) reached a level less than 0.5 mg/L (as soluble TOC), the cylinders were rinsed again, but this time the plastic bucket was placed in a water bath at proximately 65^{o}C for 24 hours. This heated rinsing procedure was repeated at least 4 times for each of the two formulations.

3.1.4 PAC content of foam cylinders

To determine the final mass of PAC in the foam cylinders, each element used to make foam was weighed before and after use. All materials were dried in a laboratory oven at 65^{o}C for 24 hours, and the dry mass of foam residue was determined. There was a small amount of PAC that remained in the plastic cups after mixing with the surfactant solution. This amount was determined by the difference between the mass of the cup after being dried in an oven at 65^{o}C for 24 hours and the initial mass before use. This amount was added to the amount of free PAC liberated in the rinse process (described below) to determine the mass of PAC that was not incorporated into the final foam.

Using glass microfiber filters (GF/F 47mm ∅ from Whatman, England), the water used in the rinsing process was filtered each time with a vacuum pressure station (Cole-parme Instrument Co., Vernon, IL). One filter was used for every three liters of water. The filters were dried in an oven at 65 ^{o}C for one day. These filters were then weighed to determine the mass of free PAC removed in the rinse water. In cases where the dried filters contained small pieces of foam, the foam particles were removed using tweezers and then the filters were weighed again to determine the exact weight of PAC.

The final mass of PAC in the rinsed foam cylinders was calculated as the difference between the initial mass of PAC mixed with the surfactant solution and the losses of PAC throughout the manufacturing and rinsing processes. In order to

determine the final percentage of PAC in the foam, all the masses of dried foam produced were added together and then divided by the mass of PAC remaining in the foam to calculate the final percent PAC by mass in the foam.

Table 3.2: Polyurethane foam formulations

Formulation	Surfactant Type	Surfactant Solution Concentration	Carbon Type	Initial Mass of PAC (g)	Way to add PAC
A	Pluronic™ P-65	30 g/L	F-300 (Calgon)	0	*
B	Pluronic™ P-65	30 g/L	F-300 (Calgon)	15	*
C	Pluronic™ P-65	30 g/L	F-300 (Calgon)	30	*
D	Pluronic™ P-65	30 g/L	F-300 (Calgon)	45	*
E	Pluronic™ P-65	30 g/L	F-300 (Calgon)	75	*
F	SDS	10 g/L	F-300 (Calgon)	45	**
G	SDS	50 g/L	F-300 (Calgon)	45	**
H	Tween® 80	1 g/L	F-300 (Calgon)	45	**
I	Tween® 80	2.5 g/L	F-300 (Calgon)	45	**
J	Tween® 80	5 g/L	F-300 (Calgon)	45	**
K	Tween® 80	10 g/L	F-300 (Calgon)	45	**
L1	Tween® 80	5 g/L	SN (Westvaco)	45	***
L2	Tween® 80	2.5 g/L	SN (Westvaco)	45	***
M	Tween® 80	5 g/L	SN (Westvaco)	45	**

* PAC added to surfactant solution

** PAC loaded with water before it was added to surfactant solution

***PAC loaded with toluene before it was mixed with water and then surfactant solution.

3.1.5 Other packing medium

Type M-2CC porous polyurethane foam cubes coated with activated carbon were obtained from Honeywell (Morristown, NJ). Each cube was approximately 5.1 cm (2 in) per side and with an average mass of 8.57 g (average of 10 samples – see

section 4.1.2). The cubes were cut in smaller cubes of approximately 1.25 cm (½ in) per side prior to use in a sorption and head loss experiments. Experiments were conducted using the Honeywell foam to determine density, moisture holding capacity, head loss, and adsorption capacity.

3.2 Sorption Studies

3.2.1 Batch sorption studies

Isotherm experiments were conducted to quantify sorption characteristics for toluene onto polyurethane/PAC foam. For batch sorption studies, foam cylinders were cut in cubes with approximately 0.5 cm sides using steel scissors.

Different amounts of foam were placed into 260 mL amber glass bottles from I-Chem (New Castle, DE), which were totally filled with a compound solution, covered with teflon-silicone septa caps (New Castle, DE), and placed in a tumbler for 48 hours. The amount of foam in each bottle ranged from 0 to 10 g, and the initial toluene concentration ranged from 10 to 400 mg/L. After 48 hours, aqueous samples were removed and the VOC concentration in the bulk liquid was measured using analytical techniques described in section 3.3.

3.2.2 Fixed bed adsorption and desorption

Experiments to determine adsorption on the filter medium were conducted using a glass column with an inner diameter of 9.9 cm. As depicted in Figure 3.2, the glass column consisted of a bottom, a top and five 25 cm sections. For adsorption and desorption experiments using foam formulation A to M, each section was filled with a 20 cm tall polyurethane foam cylinder (previously adjusted to 65% moisture content) to provide a total bed depth of one meter and a total bed volume of approximately 7.7 L. The media tested as cylinders (foam formulations A to M) swell when wet, and the diameter of the wet cylinders was approximately 0.5 cm larger than the inside of the column. Consequently, the cylinders held themselves in place once placed inside the glass column.

Compressed air from the laboratory air tap flowed through tubing to an activated carbon filter to remove unwanted contaminants. Airflow rates were measured and regulated by flow meters. Approximately 95% of the air flow was humidified by passing it through an aeration stone submerged in a 20 L glass carboy containing deionized water, and approximately 5% of the air flow was used to volatilize toluene. The two air streams entered the plenum at the bottom of the column. Small glass marbles were placed in the bottom of the column evenly to distribute air in the plenum before it entered the polyurethane foam medium. The specific compound tested was delivered by syringe pump through a glass gas-tight syringe into the air stream.

The polyurethane foam was adjusted to 65% moisture content before it was put into the column. Adsorption and desorption isotherm experiments were conducted for a variety of influent gas flow rates and different concentrations of toluene (see Table 3.3). The experiments to determine adsorption on the filter medium were conducted by setting the syringe pump and influent air flow rate at the desired levels and measuring influent and effluent compound concentrations over time until influent and effluent

concentrations were equal. The amount of material adsorbed was determined as a function of the concentration at a constant temperature.

For fix-bed adsorption and desorption experiments using Honeywell foam, a different procedure was used. A metal plate installed in the bottom of the lower glass section was used to support packing containing of 1.25 cm side foam cubes packed to a height of 1.0 m. To adjust the moisture content of the foam cubes, the column was filled with deionized water and allowed to stay in this condition for 30 minutes. Then, the column was drained by gravity. Adsorption and desorption isotherm experiments using Honeywell foam were conducted using the same influent gas flow rates and concentrations as was used for other foam formulation.

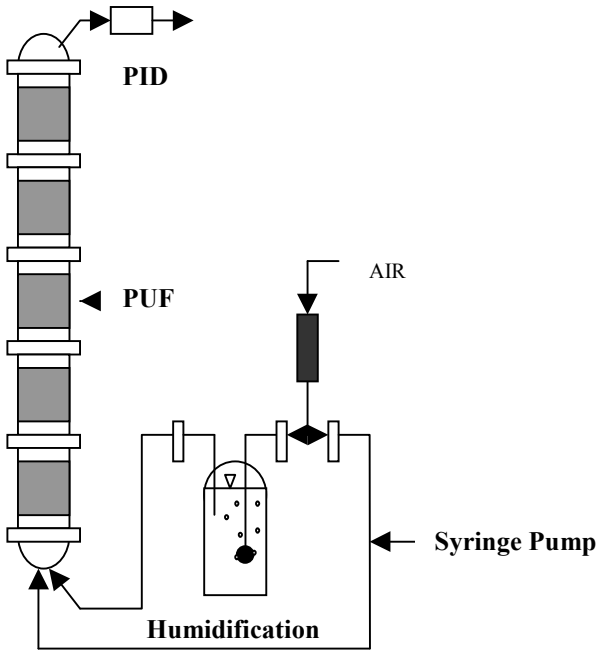

Figure 3.1: Schematic diagram of the apparatus used for fixed-bed adsorption and desorption experiments

Fixed-bed desorption studies were conducted after each adsorption experiment. In this case, the syringe was removed from the syringe pump to stop contaminant loading, and unpolluted air moved through the column continuously. The contaminant concentration in the effluent flow was measured over time until no concentration of the compound tested was detected.

The mass of contaminant adsorbed or desorbed to the foam material was calculated giving consideration to the fact that a portion of the contaminant was absorbed by water associated with the wet packing media. The mass of water present (65% moisture content for experiments using foam cylinders and approximately 30% for Honeywell foam) was assumed to be equilibrium with the influent gas-phase concentration at the end of each adsorption experiment when the influent and effluent contaminant concentrations were equal and unchanging over time. Henry's Law (see values in Table 1.1) was used to calculate the concentration of contaminant in the

aqueous phase. The mass of contaminant in the aqueous phase was calculated by multiplying the concentration by the mass of water present in the wet foam. The mass of VOC adsorbed by the foam was calculated as the total mass of contaminant sorbed minus the mass absorbed by the water. The same procedure was applied to obtain the mass of contaminant desorbed from the foam.

Table 3.3: Flow rates and compound concentration for fixed-bed adsorption and desorption experiments using toluene

Gas Concentration (mg/L)	Gas Concentration (ppm_v)	Empty Resident Time (seconds)
2.651×10^{-2}	6.99	20
2.651×10^{-2}	6.99	60
2.651×10^{-1}	69.9	20
2.651×10^{-1}	69.9	60
3.794×10^{-1}	100	20
1.897	500	20
2.651	699	20
2.651	699	60

3.3 Analytical Techniques

3.3.1 Total organic carbon (TOC)

The total organic carbon (TOC) content of water used to rinse foam after manufacture were analyzed following the Standard Methods for Examination of Water and Wastewater (APHA, 1999) using a TOC-5050A from Shimadzu (Kyoto, Japan). A calibration curve was prepared using various dilutions of a standard prepared by adding 2.125 g of potassium hydrogen phthalate (Sigma, St. Louis, MO) to one liter of deionized water; (this is equivalent to 1000 mg/L soluble TOC).

For analysis of samples, 20 mL of the rinse water was filtered using a 0.45 μm syringe filter (Millex, Bedford, MA) and placed into three 4 mL vials. Correlation curves for the TOC content of various Pluronic P-65 and Tween 80 surfactant solutions was made to know the concentration of surfactant desorbed by the foam in the rinse process. Results for these experiments are presented in Appendix 1.

3.3.2 Dry density, wet density, and porosity tests

Experiments were conducted to determine the dry and wet density of the various media. The wet and dry mass, and volume of several cylinders for each characterization were measured. For density tests, foam cylinders were placed in a laboratory oven for at least for 24 hours at 65 ^{o}C the dimensions of each cylinder were measured using a ruler, and the mass was measured using an analytical balance. Density was calculated by dividing mass by volume. Because most of the foam formulations were hydrophilic and increased in size when wet, density was also

determined for wet packing media. After the dry tests, the foam cylinders were wetted to 65% moisture content using deionized water. Then, volume and mass measurements were repeated. The mathematical average of several cylinders from the same characterization was calculated and reported.

For Honeywell foam, a known amount of foam was placed in a glass column, and the volume of foam was measured. The volume of deionized water required to completely fill all the air spaces was recorded. The volume of water is considered to be equal to the void spaces. The porosity was calculated as the volume of void spaces divided by the sum of foam volume and void spaces volume The water was allowed to stay in the column for 30 minutes, and then the column was drained by gravity. The volume of water drained by gravity was measured. The difference between the volume of water added to the column and the volume drained by gravity was calculated. The mass of water remaining in the column was divided by mass of the dry foam in the column and was considered to represent the moisture holding capacity. Resulting data is reported in section 4.1.3.

3.3.3 Head loss test

A head lost testing apparatus was constructed using a section of PVC pipe, 116.8 cm (46 in) long with a 10.2 cm (4 in) diameter and two 10.2 cm (4 in) diameter end caps. Two hose barb connectors were installed at the extremes of the PVC pipe to connect a water manometer (see Figure 3.2). For head loss tests of foam manufactured for testing (Formulation A to M), head loss was determined using foam cylinder monoliths (rather than foam cubes as were used for Honeywell foam). Five foam cylinders were placed inside of the pipe while compressed air from the laboratory air supply was allowed to pass through the bed of polyurethane foam (at 65% moisture content). A flow meter was installed at the influent air tubing to measure and regulate the airflow rate. A water manometer was used to measure pressure drop across the foam medium at various flow rates. Head loss was recorded to the nearest 1 mm.

For Honeywell foam, a glass column (similar to those described in section 3.2.2) was used to conducted head loss test. A metal plate was installed in the bottom of the lower glass section supporting 1.25 cm side foam cubes packed to a height of 1 m. To adjust the moisture content of the foam cubes, the column was filled with deionized water and allowed to stay in this condition for 30 minutes. Then, the column was drained by gravity. A flow meter was installed at the influent air tubing to measure and regulate the airflow rate. A water manometer was used to measure pressure drop across the foam medium at various flow rates. Head loss was recorded to the nearest 1 mm.

3.3.4 HPLC analysis

For isotherm experiments, aqueous samples were collected using a 5 mL glass syringe (Hamilton, Reno, Nevada), passed through a 0.45 μm syringe filter (Millex, Bedford, MA), and placed in amber glass sample vials. Aqueous VOC concentrations were measured using a Hewlett Packard series 1090 HPLC equipped with an Agilent Eclipse XDB-C18 5μm and 4.6×250 mm column (Palo Alto, CA). The injection volume was 50.0 μl at 83.3 μL/min draw speed. For toluene measurements, the mobile

phase was 85% methanol and 15% water, the oven temperature 30 ^{o}C, and pump flow rate 1.0 mL/min. The detector wavelength was set at 260 nm, for toluene. Calibration curves were made using certified standards from Supelco (Bellefonte, PA). Retention time for toluene was 5.4 minutes. All samples were analyzed immediately after collection or were refrigerated at 5 ^{o}C prior to analysis.

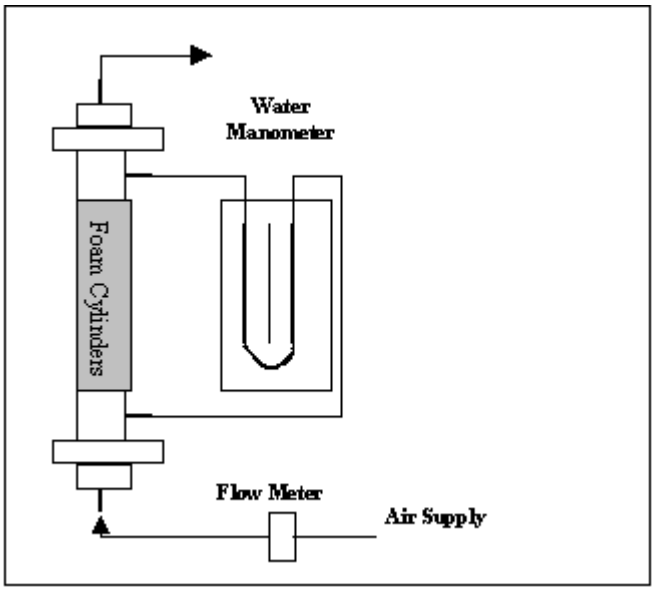

Figure 3.2: Schematic of head loss testing apparatus

3.3.5 Gas chromatography analysis

Aqueous VOC concentrations was also measured using a Hewlett Packard 6890 series gas chromatograph, equipped with a purge and trap autosampler and a DB-624 Special Analysis Column (Capillary 60 m × 320 um × 1.80 um nominal) from Hewlett Packard. Aqueous samples were placed in purge and trap autosampler and concentrator (series 2016 and 3000, respectively, from Tekmar, Mason, Ohio). Helium was used to purge the VOC out of the liquid solutions for 8 minutes, desorption time was 2 minutes, and the bake time was 10 min. A split injection was used, with a 1:30 split ratio, and 59.6 mL/min slip flow rate of helium. Oven temperature was held at 200 ^{o}C for 10 minutes. A flame ionization detector (FID) was used to measure toluene. The injector and detector temperatures ware set at 225 ^{o}C with hydrogen flow rate of 40 mL/min, and airflow rate of 200 mL/min. Toluene eluted with a retention time of approximately 5.8 minutes. An example calibration curve is show in Figure 3.3.

3.3.6 Gas-phase analysis by PID

A Photo-Ionization Detector (PID) (MiniRAE 2000 series PGM-7600, RAE, Sunnyvale, CA), was used to measure the VOC concentration at the inlet and outlet. MiniRAE 2000 portable VOC monitor is a compact online monitor designed as a broadband VOC gas monitor for work with hazardous compounds. The PID was

calibrate using compressed nitrogen gas (BOC, Port Allen, LA) as zero gas, and compressed nitrogen containing MEK at 198 ppm_v or 1080 ppm_v (certified calibration standard, BOC, Port Allen, LA) as span gas. For toluene measurement, a conversion factor obtained from the manufacturer was used to obtain the toluene concentration.

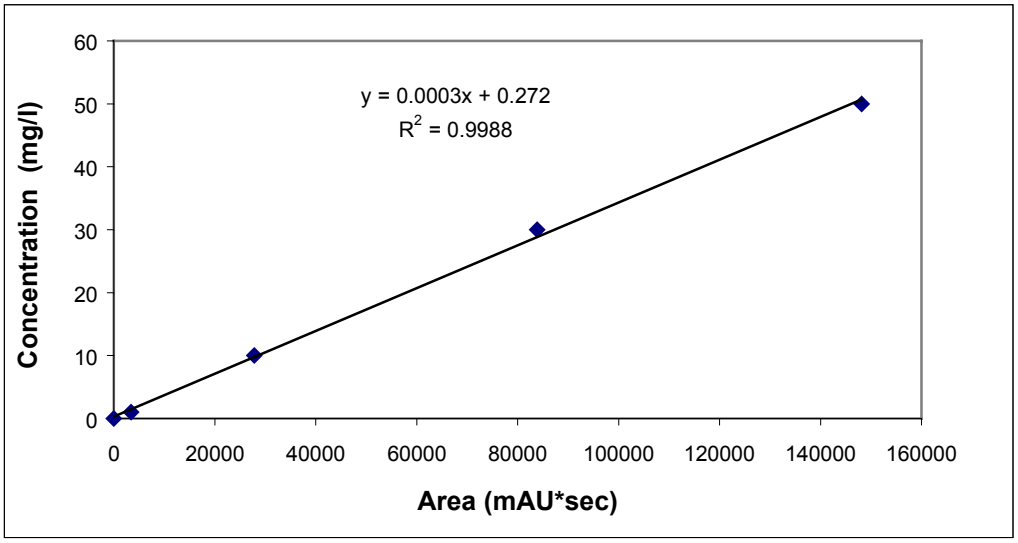

Figure 3.3: Calibration curve for toluene using GC

CHAPTER 4 RESULTS AND DISCUSSION FOR PRELIMINARY EVALUATION

Section 4.1 of this chapter contains results related to rinsing of the polyurethane foam that was manufactured. Section 4.2 contains information related to dry and wed density measurements. Section 4.3 contains results of head loss experiments. Section 4.4 contains results of batch and fixed-bed sorption experiments. Section 4.5 contains preliminary conclusions and summarizes the rational for selecting two packing media for further characterization.

4.1 Foam Rinsing Experiments

4.1.1 Total organic carbon (TOC)

To quantify the mass of surfactant removed from the foam cylinders during the rinsing process, TOC was measured in the water used to rinse foam formulations A, C, D, E, J, and M. As an initial step, the relationships between Pluronic^{TM} P-65 and Tween 80 surfactant solution concentrations and soluble TOC were determined (see Appendix 1). For all formulations tested which used P-65 as the surfactant, approximately 22 rinsing cycles were needed to bring the TOC concentration to below 0.5 mg/L. Figures 4.1, 4.2, 4.3, and 4.4 show the concentration of P-65 surfactant solution in terms of TOC in the rinsing process for foam formulations A, C, D, and E respectively. The figures also show the concentration of surfactant removed. The surfactant concentration was calculated using the measured TOC concentration and the experimentally determined relationship between TOC and surfactant concentration. This calculations procedure explicitly assumes that all TOC in solution was due to surfactant.

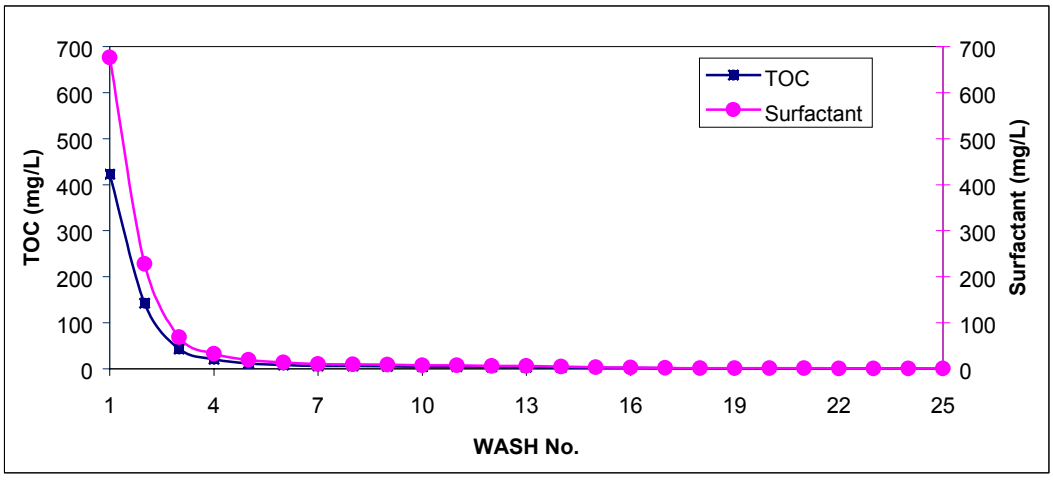

Figure 4.1: Measured TOC concentration and calculated surfactant concentration during the rinsing process for foam formulation A

In the foam rinse procedure, the P-65 surfactant concentration of the first rinse water was approximately 676 mg/L for foam with no activated carbon (Formulation A) and only 22 mg/L for foam with 36.4% PAC by mass (Formulation E). Desorption

of free P-65 surfactant during the rinse process for different foam formulations is summarized in Table 4.1. As clearly indicated by these data, the mass of P-65 surfactant recovered in the rinse water decreased as the mass of PAC in the formulation increased. 102% of the surfactant was recovered in formulation A (no PAC), while only 8.7% was recovered in foam formulation E (75 g PAC per cylinder) This is likely due to surfactant adsorption to the activated carbon during the manufacturing process.

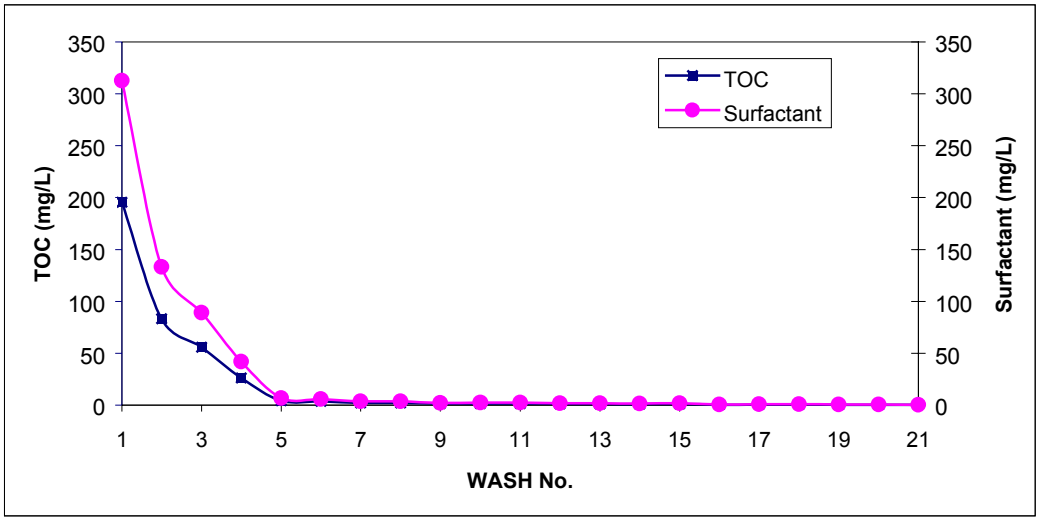

Figure 4.2: Measured TOC concentration and calculated surfactant concentration during the rinsing process for foam formulation C

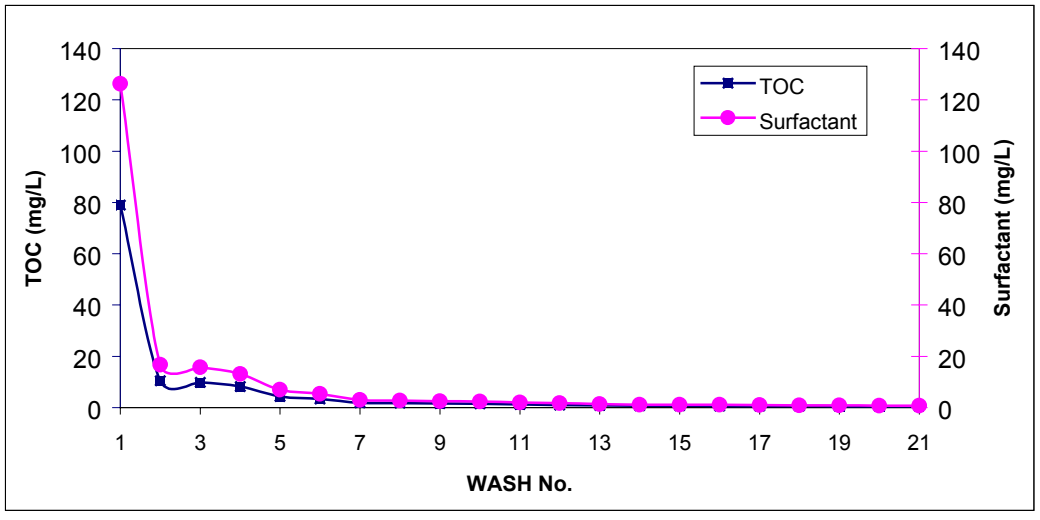

Figure 4.3: Measured TOC concentration and calculated surfactant concentration during the rinsing process for foam formulation D

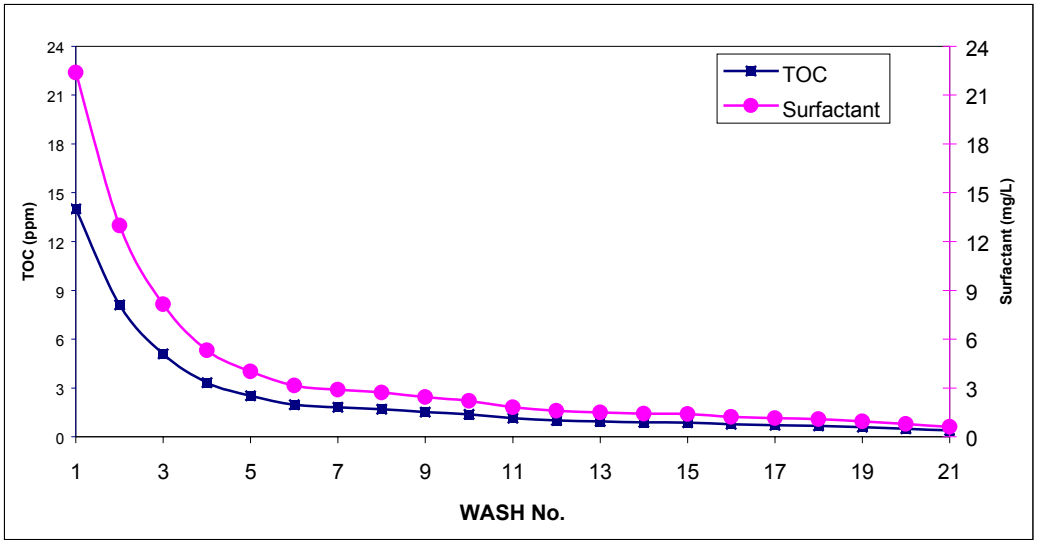

Figure 4.4: Measured TOC concentration and calculated surfactant concentration during the rinsing process for foam formulation E

Table 4.1: Free P-65 surfactant desorbed during the rinsing process

FOAM FORMULATION	FREE SURFACTANT OUT IN THE RINSING PROCESS				
	MASS TOC REMOVED (mg)	MASS SURFACTANT REMOVED (mg)	MASS SURFACTANT REMOVED PER CYLINDER (mg)	CALCULATED INITIAL MASS OF SURFACTANT PER CYLINDER (mg)	% OF P-65 DESORBED
A	6298	10048	2010	1968	102
C	3469	5534	1107	2025	54.7
D	456	727	375	1867	20.1
E	493	787	157	1808	8.7

The TOC concentration was measured in rinsing water from foam cylinders of formulation J and M, which were manufactured using Tween® 80 surfactant. After surfactant remaining in the foam rinse water was less than 0.5 mg/L of soluble TOC, the foam cylinders were rinsed again, but this time, the plastic bucket was placed in a water bath at approximately 65^{o}C for 24 hours. Figure 4.5 shows the results of Tween® 80 surfactant desorption in the rinsing process for formulation J. The low TOC concentration in the rinse water for wash 5 may be due to analytical error. There is a clear increase in free surfactant desorption when the foam cylinders were submerged in hot water. A similar result was found for foam formulation M when it was rinsed with hot water see Figure 4.6. The total mass desorbed during the first rinse with hot water is twice the mass with water at ambient temperature.

Table 4.2 summarizes desorption of surfactant in formulation J and M. The total percent of surfactant desorbed increased considerably in comparison to that from formulations C, D, and E. There are several likely reasons for this effect. First, the PAC was loaded with deionized water before it was mixed with the surfactant during foam manufacture. The association of water with sorption sites may have prevented surfactant sorption. Second the foam cylinders were rinsed 4 times with hot water. The higher temperature may have increased surfactant desorption. A third likely reason for the differences between final percent of surfactant desorbed for foam formulations J and M is that those were made with a different type of activated carbon which likely have different sorption capacity. A fourth potential reason is that Tween 80 was used instead of Pluronic P-65. Tween 80 has a lower molecular weight than PLURONIC P-65 (see Table 3.1) does, and lower molecular weight compounds may desorb more readily.

Table 4.2: Free Tween 80 surfactant desorbed

FOAM FORMULATION	FREE SURFACTANT OUT IN THE RINSING PROCESS				
	MASS TOC REMOVED (mg)	MASS SURFACTANT REMOVED (mg)	MASS SURFACTANT REMOVED PER CYLINDER (mg)	CALCULATED MASS OF SURFACTANT PER CYLINDER (mg)	% OF P-65 SURFACTANT DESORBED
J	6793	10596	1766	332	533
M	1329	2107	301	373	81

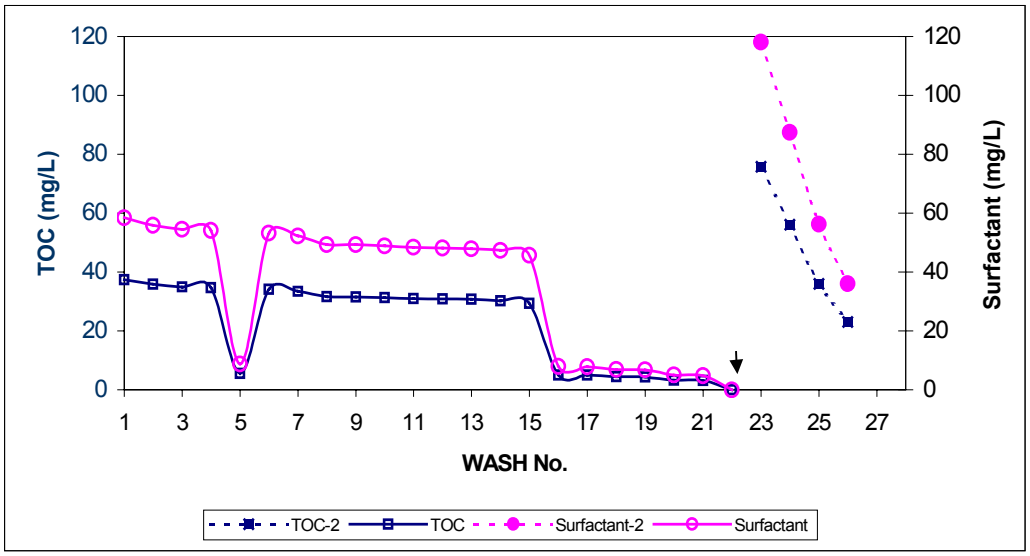

Figure 4.5: TOC and surfactant concentration removed during the rinsing procedure for foam Formulation J. Arrow indicates time of temperature increase.

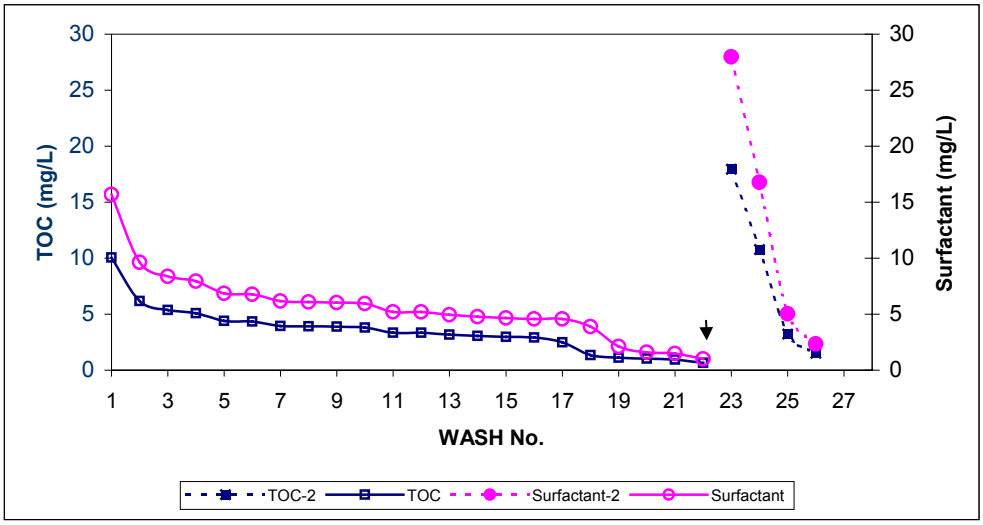

Figure 4.6: TOC and surfactant concentration removed during the rinsing procedure for foam Formulation M. Arrow indicates time of temperature increase.

4.1.2 Final percent of PAC

A portion of the PAC initially present in the foam cylinders was removed during the rinsing procedure. The mass of PAC and the mass of foam removed during the rinsing procedure for foam formulations C and E are depicted in Figures 4.7 and 4.8, respectively. The mass of PAC present in the rinse water decreased appreciably with each subsequent washing. For example, with foam formulation E, the medium with the highest PAC content, approximately 170 mg of PAC was removed during the first rinse and only 10 mg was removed during the 15th rinse (see Figure 4.7). This is likely due to the fact that PAC not fully incorporated into the foam matrix was removed because of shear stress during washing.

To determine the final amount of PAC in the foam cylinders, each element used to make foam was weighed before and after be used. The final percent PAC (by mass) for each of the foam formulations is listed in Table 4.3. As can be seen from the data, the percent PAC ranged from 0 to 36.4% for the formulations tested. A table summarizing all measurements used to calculate the parameters in Table 4.3 can be found in Appendix 2.

Table 4.3: Final PAC content after rinsing

Formulation	Percent PAC (by mass)
A	0
B	10.0
C	19.2
D	26.8
E	36.4
J	27.9
M	29.9

Results for foam the formulation L1 are not shown in Table 4.3 because the resulting foam cylinders were very small and dense compared to other foam formulations (see table 4.4), and based on visual observation, the pores were comparatively small and not well interconnected. Apparently, the incorporation of toluene to Westvaco PAC by adsorption before it was mixed with surfactant generated a barrier that did not allow the surfactant solution to mix properly with the prepolymer, and the resulting foam cylinders could expand in size to as great of an extent as with other foam formulations. The formulation L2 was not really different than Formulation L1, even though Formulation L2 had the twice the amount of water than did L1. Both were discarded.

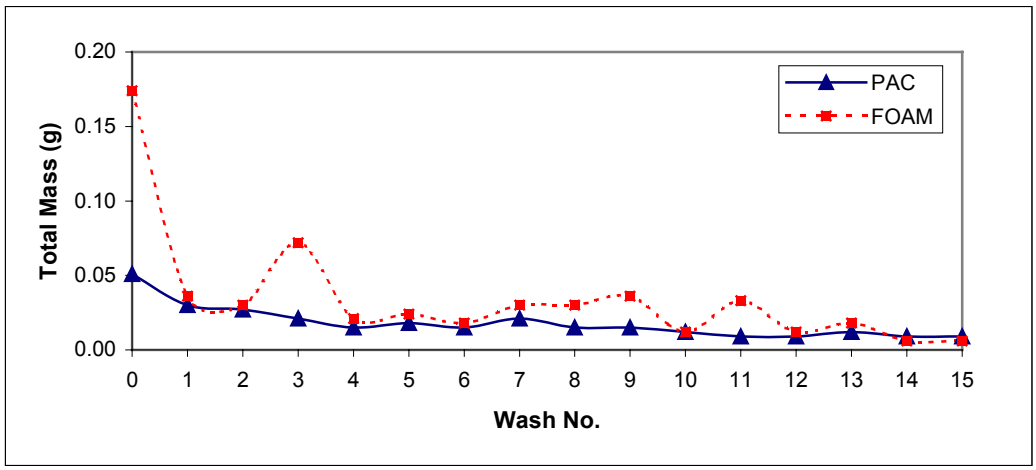

Figure 4.7: Mass of PAC and foam removed from 5 cylinders in the rinsing procedure for Formulation C

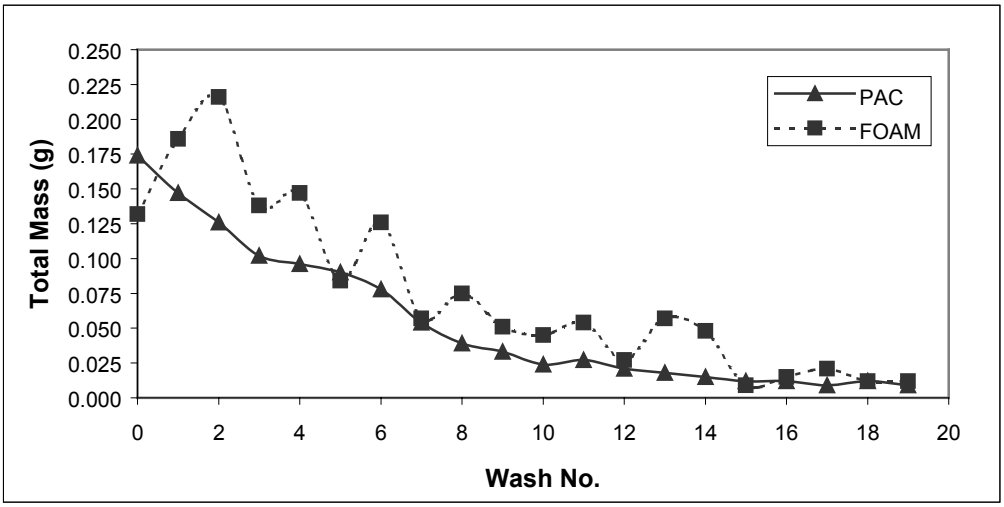

Figure 4.8: Mass of PAC and foam removed from 5 cylinders in the rinsing procedure for Formulation E

4.2 Dry Density, Wet Density, and Porosity Test

For most of the foam formulation, both dry and wet density were determined. The wet and dry mass and volume of several cylinders for each characterization was measured, and a mathematical average was calculated. The data collected is shown in Table 4.4. Wet density measurements for all tested except for Honeywell were determined at 65% moisture content. This corresponds to a condition where the material was fully hydrated (the material is hydrophilic) but with little free water filling the pore space.

Holding capacity test for Honeywell foam was performed to determine the maximum moisture content that the hydrophobic material is able to hold under the conditions tested. Results indicate that the maximum moisture content values do not exceed 30%. The porosity test results indicate that the void volume was approximately 96% of the total volume for the foam cubes placed in the column. The material bulk density was calculated (using data obtained from the porosity test) to be approximately 52 g/cm^3 at 30% moisture content for the cubed medium as it was packed in the columns.

Table 4.4: Dry and wet density for various foam formulations

Formulation	Dry Density (g/L)	Wet Density (At 65% moisture) (g/L)
A	82.4	137.2
C	89.3	157.9
D	94.9	182.1
F	84.6	170.6
G	88.9	176.9
H	75.5	157.1
J	107.6	170.2
K	84.1	164.9
L	200.7	525.7
M	118.8	258.1
Honeywell	83.3	100.2*

*Approximately 20% moisture content (water holding capacity)

4.3 Head Loss Test

Head loss through one meter of polyurethane foam packing material was measured at air surface loading rates ranging from 0 to 400 $m^3m^{-2}hr^{-1}$ using foam made using final PAC concentrations ranging from 0 g/L to 36.4 g/L. The results presented in Figure 4.9 clearly show that foam made with 0 to 10.0% PAC had less head loss than foam made with more. For all of the formulations, the head loss was considerably lower than that for conventional organic packing media such as compost (Leson and Winer, 1991).

Figure 4.10 shows the differences between head loss for foam formulations D, J, and M. AS expected based on the observations and density measurements (see section 4.2) foam formulation M had a higher head loss than other foam cylinders.

Honeywell foam had a low head loss, even though it was necessary to use two metal support plates to support the foam cubes. The maximum value for head loss did not exceed 0.1 cm H_20 for surface loading rate less than 300 m^3/m^2*hr. This head loss is less than for any of the other media tested and considerably less than conventional biofilter packing media is. It should be noted, however, that the head loss across columns containing other types of foam media was measured under conditions where the foam cylinders completely filled the column. Had those been cut into cubes and then packed into the column in the same manner as the Honeywell media, the head loss would likely have been lower.

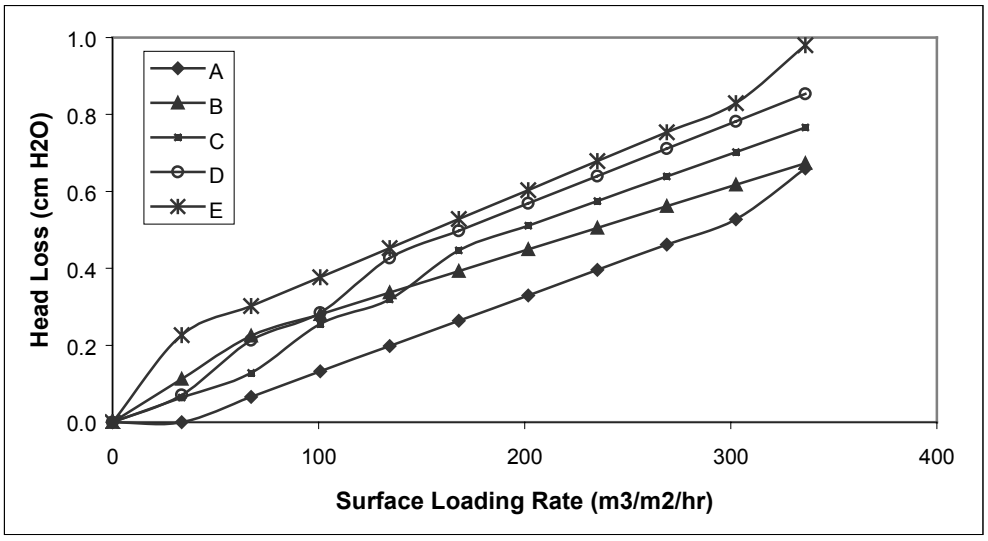

Figure 4.9: Head loss across 100 cm packing of polyurethane foam formulations A, B, C, D, and E at various surface-loading rates

4.4 Adsorption Test

Fixed bed adsorption and desorption experiments were conducted using a glass column reactor to quantify sorption to the filter media under dynamic conditions. Foam formulations A, C, D, J, M and Honeywell foam were used to conduct toluene adsorption and desorption experiments. The total mass adsorbed by the water and

adsorbed by the media was calculated by subtracting the total mass of toluene in the effluent from total influent mass. The following section shows the breakthrough graphics for each formulation tested grouped by empty bed resident time, for different influent concentrations. Also, Appendix 4 shows each test individually.

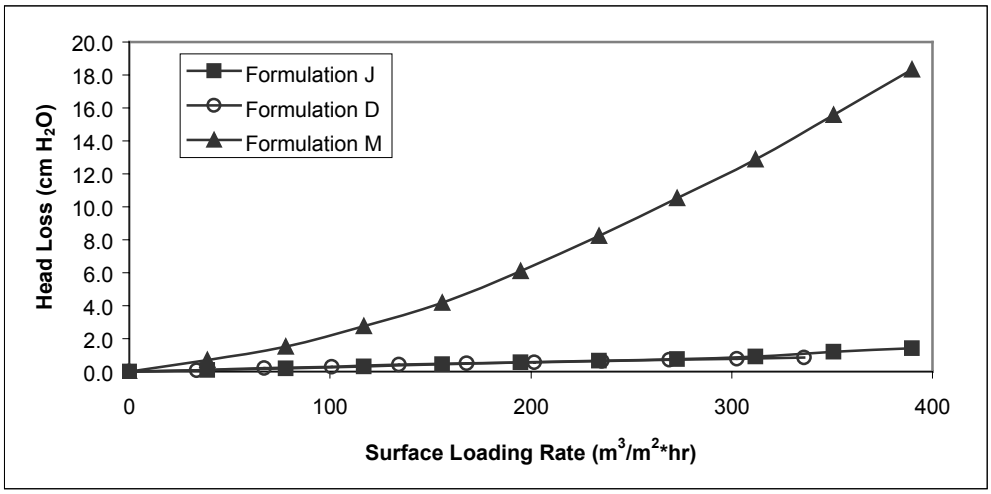

Figure 4.10: Head loss across 100 cm packing of polyurethane foam formulations D, J, and M at various surface-loading rates

Figures 4.11 and 4.12 present the adsorption data for foam formulation A at different influent concentrations and empty bed resident times (EBRTs). Table 4.5 summarizes the test conditions and results. As can be seen from the figures and table, 10% of the influent toluene concentration was observed in the effluent after 5 min and 7 min for influent concentrations of 6.9 ppm_v and 69.9 ppm_v, respectively, with a EBRT of 20 seconds. For an EBRT of 60 seconds, it took 8 min and 11 min for 10% breakthrough when the initial concentration was 6.9 ppm_v and 69.9 ppm_v, respectively, with an EBRT of 20 seconds. For EBRT of 60 seconds, it took 8 min and 11 min for 10% breakthrough when the initial concentration was 6.9 ppm_v and d 69.9 ppm_v, respectively.

Figures 4.13 and 4.14 present desorption of toluene by foam formulation A. As can be seen from the figures the effluent toluene concentration decrease rapidly during the initial period following removal of toluene from the influent gas stream. Subsequently, there was a less rapid decrease in the toluene concentration. For example, it took only 80 min for the dimensionless effluent concentration to decrease from 1.0 to 0.1, while it took a additional 320 min to reach 0.05 for an EBRT of 20 seconds and an initial toluene concentration of 69.9 ppm_v (see figure 4.13).

A similar patter was observed for an EBRT of 60 seconds. For initial toluene concentrations of 6.9 and 69.9 ppm_v, it took 39 min and 78 min, respectively, for the dimensionless concentration to decrease from 1 to 0.1. Likewise, it took an additional 20 min and 159 min to decrease to 0.05 for initial concentrations of 6.9 and 69.9 ppm_v, respectively.

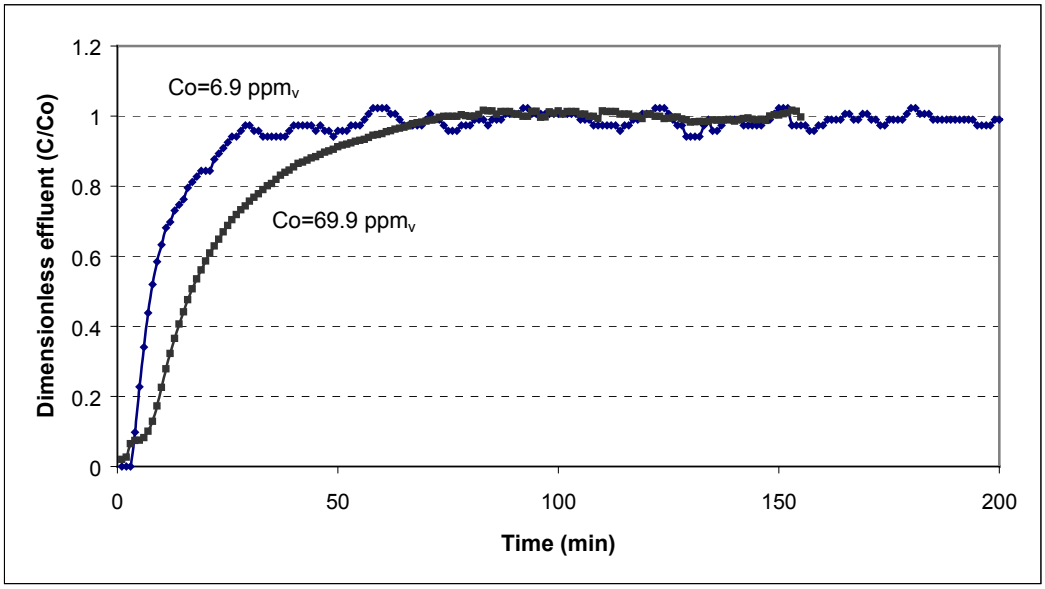

Figure 4.11: Adsorption of toluene by foam formulation A with 20 seconds EBRT

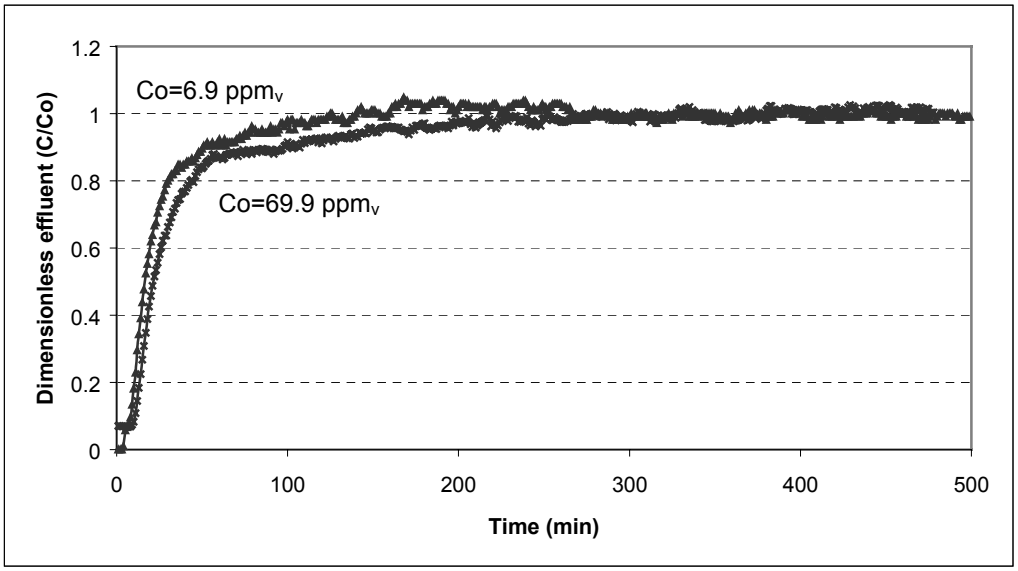

Figure 4.12: Adsorption of toluene by foam formulation A with 60 sec. EBRT

As shown in the Tables 4.5 and 4.6, the mass of toluene adsorbed and desorbed was calculated for each toluene concentration and EBRT combination tested. For an EBRT of 20 seconds and toluene concentration of 69.9 ppm_v, the mass of toluene sorbed (95.9 mg) and the desorbed (94.4 mg) are within 1.6% one another. For an EBRT of 60 seconds and toluene concentration of 6.9 ppm_v the mass of toluene adsorbed (8.77 mg) and the desorbed (6.8 mg) had a difference of 1.97 mg of toluene. For an EBRT of 60 seconds and toluene concentration of 69.9 ppm_v, the mass of toluene adsorbed (81.5 mg) and the desorbed (87.3 mg) are within 5.6% one another.

Table 4.5: Adsorption test conditions and results for foam formulation A with toluene

EBRT (sec.)	Influent Gas concentration (ppm_v)	Total Influent Mass (mg)	Mass in effluent (mg)	Total Mass Adsorbed and Absorbed (mg)	Total Mass Adsorbed* (mg)
20	6.9	358	351	7.5	7.43
20	69.9	909	813	96	95.36
60	6.95	171	163	8.8	8.73
60	69.5	898	811	81	80.4

* Calculated using Henry's law and the mass of the water to quantify the mass of toluene absorbed in the water.

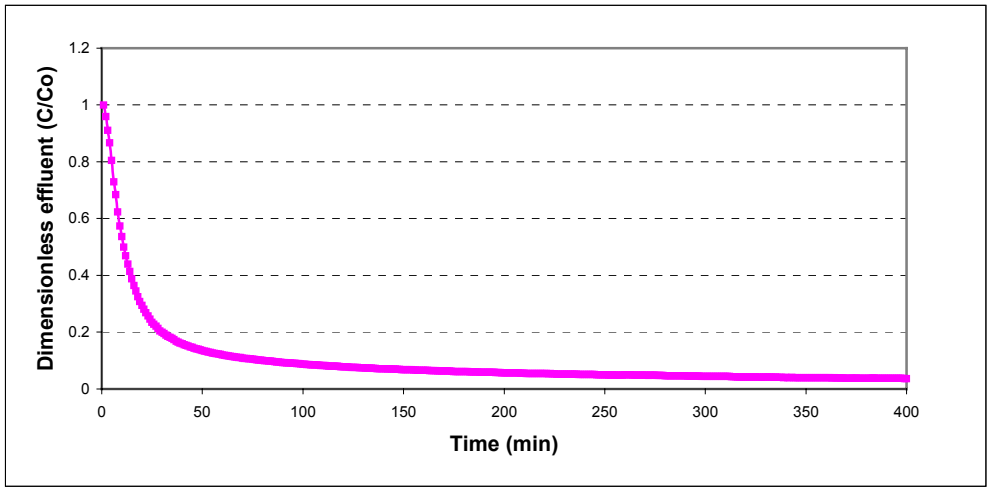

Figure 4.13: Desorption of toluene in foam formulation A, 20 sec. EBRT. Co = 69.9 ppm_v

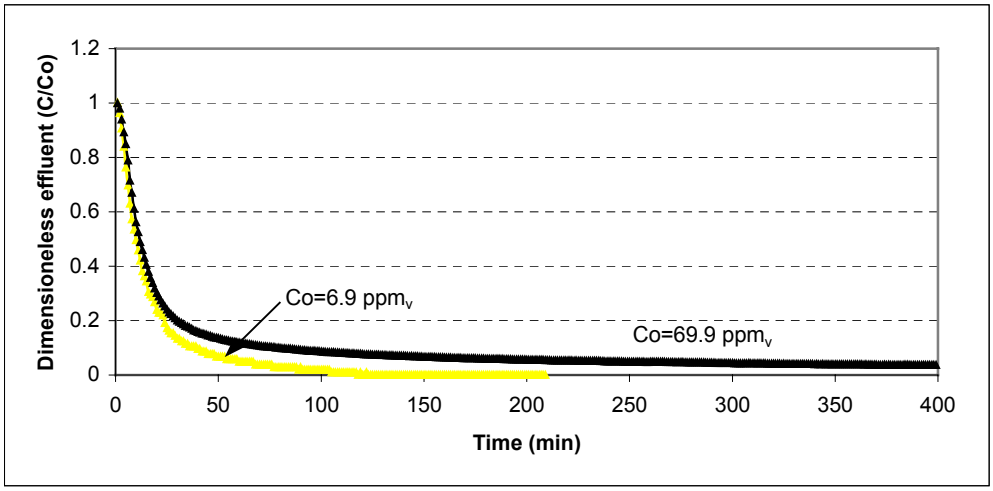

Figure 4.14: Desorption of toluene in foam formulation A, 60 sec. EBRT

Table 4.6: Desorption test conditions and results for foam formulation A

EBRT (sec.)	Initial Gas Concentration (ppm_v)	Total Mass Desorbed (mg)
20	69.9	94.9
60	6.95	6.8
60	69.5	87.3

Figures 4.15 and 4.16 depict the performance of packing material type C to toluene adsorption and desorption for fixed bed tests at 20 seconds EBRT, and an influent gas concentration of 69.9 ppm. For adsorption, the total influent mass of toluene was 4227 mg, the total effluent mass was 4048 mg, and the total mass sorbed was calculated to be 179 mg. 10% breakthrough was reached at 7 min. The total mass desorbed was 199 mg, and 94 min was necessary to decrease the effluent dimensionless concentration from 1.0 to 0.1. The mass sorbed and the mass desorbed are within 4.2% of one another. Several other fixed bed tests were made with this type of foam, but the data are not shown

Adsorption data for foam formulation D in a fixed-bed column at different influent concentrations and EBRTs are presented in the Figures 4.17, and 4.18, followed by Table 4.7 that summarizes the test conditions and results. As can be seen from the figure and table, 10% of the influent toluene concentration was observed in the effluent after 7 min for influent concentrations of 69.9 ppm_v with an EBRT of 20 seconds. For an EBRT of 60 seconds, it took 13 min and 23 min for 10% breakthrough when the initial concentration was 6.9 ppm_v and 69.9 ppm_v, respectively.

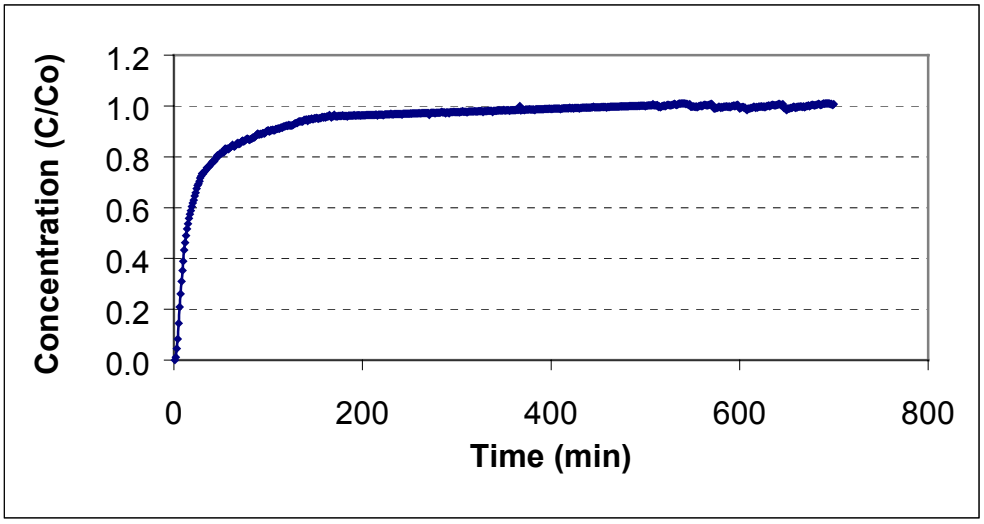

Figure 4.15: Adsorption of toluene by foam formulation C with 20 sec. EBRT.

Figures 4.19 and 4.20 present desorption data by toluene for foam formulation D for 20 and 60 sec. EBRT, and Table 4.8 summarizes the experimental results. As can be seen from the figures the effluent toluene concentration decreased rapidly during the initial period in a similar way that did Formulations A and C. Subsequently,

there was a less rapid decrease in the toluene concentration. For example, it took only 63 min and 100 min for the dimensionless effluent concentration to decrease from 1.0 to 0.1 at initial influent concentration of 6.95 ppm_v and 69.51 ppm_v, respectively. And it took additional 173 and 731 min to reach 0.05 for an EBRT of 20. A similar pattern was observed for an EBRT of 60 seconds. For initial toluene concentration of 6.95 and 69.5 ppm_v, it took 772 min and 234 min, respectively.

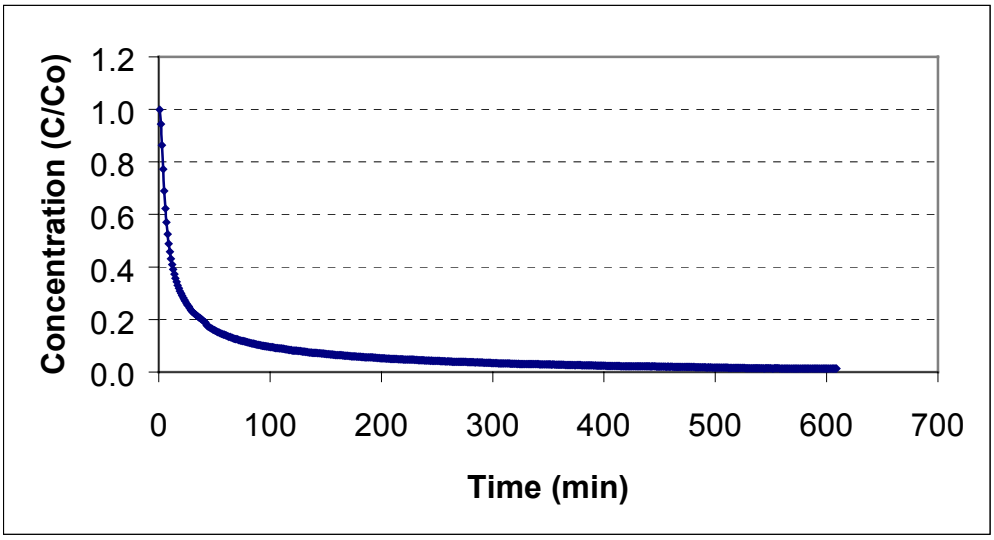

Figure 4.16: Desorption of toluene by foam formulation C with 20 sec. EBRT.

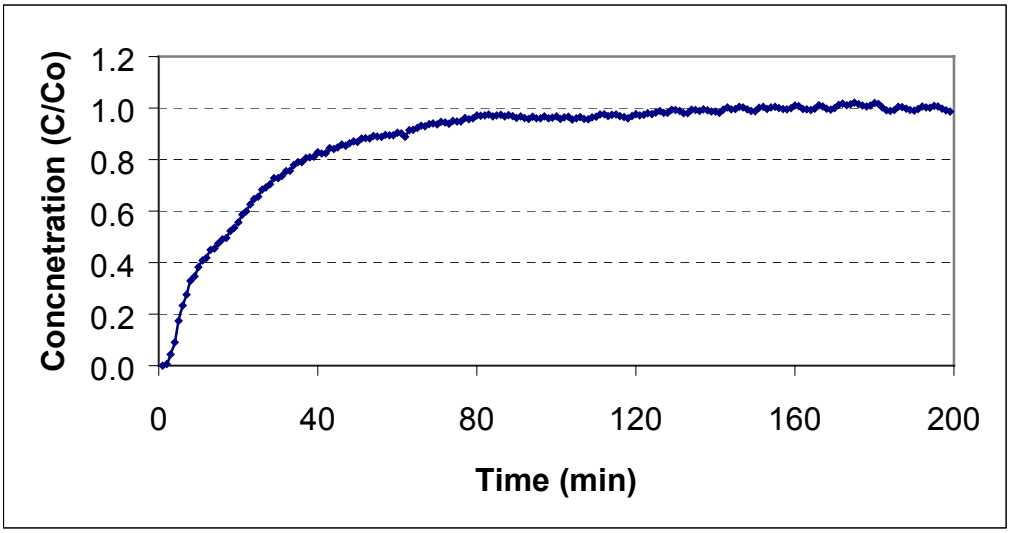

Figure 4.17: Adsorption of toluene by foam formulation D with 20 sec. EBRT and C_o = 69.9 ppm_v

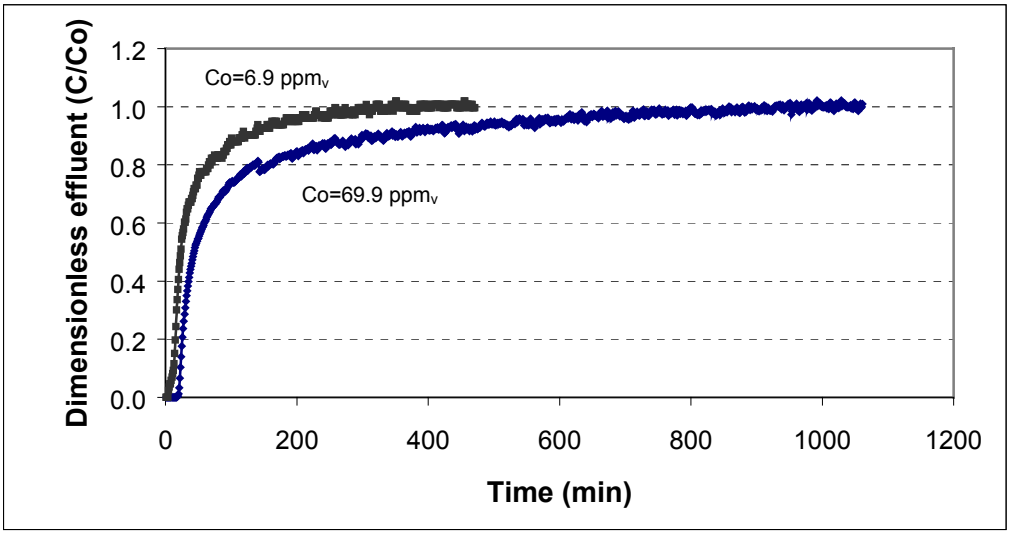

Figure 4.18: Adsorption of toluene by foam formulation D with 60 sec. EBRT

Table 4.7: Adsorption test conditions and results for foam formulation D

EBRT (sec.)	Gas Concentration (ppm_v)	Total Influent Mass (mg)	Mass in Effluent (mg)	Total Mass Adsorbed (mg)	Mass Adsorbed * (mg)
20	69.9	1395	1171 mg	224	223.1
60	6.95	101	84.8	16.2	16.0
60	69.5	2154	1919	235	233.7

*Calculated using Henry's law and the mass of the water to quantify the mass of toluene absorbed in the water.

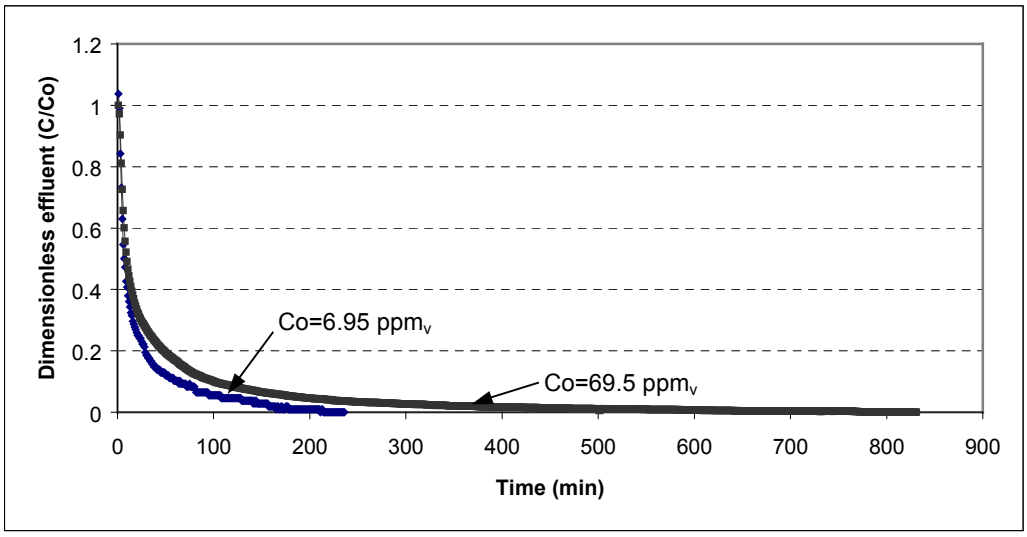

Figure 4.19: Desorption of toluene by foam formulation D, with 20 sec. EBRT.

As shown in Tables 4.7 and 4.8 the mass of the toluene adsorbed and desorbed was calculated for each toluene concentration and EBRT combination tested. For EBRT 20 seconds and toluene concentration of 69.5 ppm_v, the mass of toluene adsorbed (224 mg) and the desorbed (2345 mg) are within 4.5% one another. For an EBRT 60 seconds and toluene concentration of 6.95 ppm_v the mass of toluene sorbed (16.2 mg) and the desorbed (25.4 mg) have a different of 9.2 mg of toluene. For an EBRT 60 seconds and toluene concentration of 69.9 ppm_v the mass of toluene sorbed (235 mg) and desorbed (248 mg) are within 5.8% of one another.

Formulation J, which used Tween 80 surfactant and Calgon PAC, was analyzed by fixed-bed adsorption and desorption under similar conditions. Its adsorption breakthrough is represented in Figures 4.21 and 4.22. Figure 4.21 test conditions were 60 seconds EBRT and 6.95 ppm_v influent toluene. On the other hand, Figure 4.22 depicts results for test conditions of 20 seconds EBRT and 99.8 ppm_v influent toluene concentration. The total mass sorbed in each test was 10.2 mg and 188 mg respectively. The times necessary to reach 10% breakthrough were 20 min and 8 min for influent concentrations of 6.95 and 99.8 ppm_v, respectively.

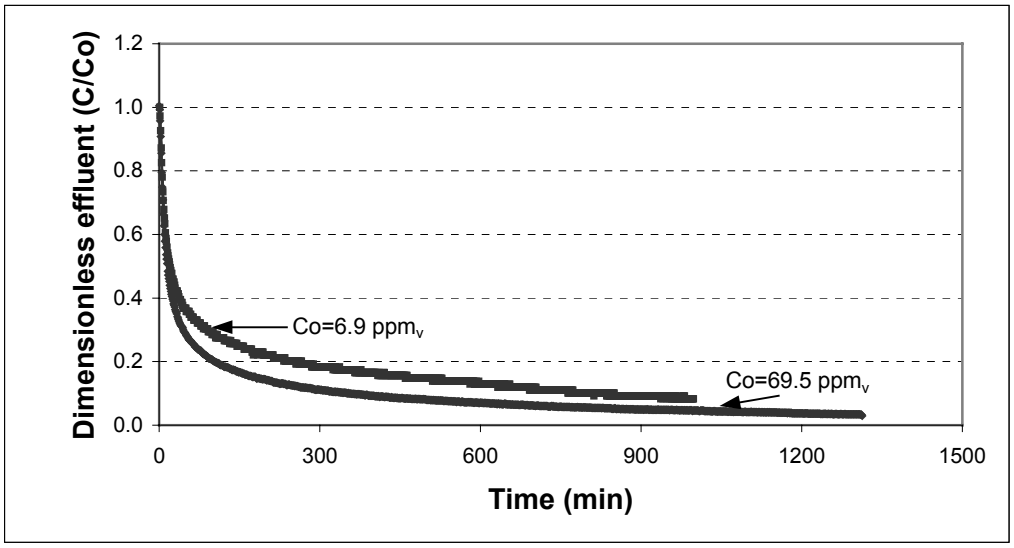

Figure 4.20: Desorption of toluene by foam formulation D with 60 sec. EBRT.

Table 4.8: Desorption test conditions and results for foam formulation D

EBRT (sec.)	Gas Concentration (ppm_v)	Total Mass Desorbed (mg)
20	6.95	15.6
20	69.5	235
60	6.95	25.4
60	69.5	248.

Figure 4.23 depicts desorption of toluene in foam formulation J with 20 second EBRT and initial toluene concentration of 99.8 ppm_v. The total masses desorbed were

166 mg, and 181 mg in duplicate experiments. As can be seen from Figure 4.23, the effluent toluene concentration decreased rapidly during the initial period following removal of toluene from the influent gas stream. Subsequently, there was a less rapid decrease in the toluene concentration. For an EBRT of 20 seconds and initial toluene concentration of 99.8 ppm_v, it took 69 min and 81 min for the dimensionless concentration to decrease from 1 to 0.1. Likewise, it took an additional 42 min and 69 min to decrease to 0.05.

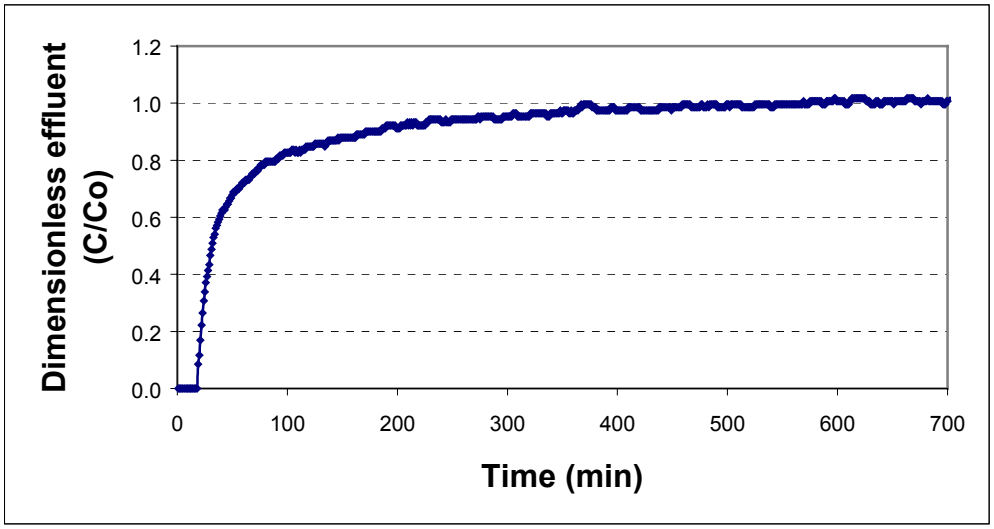

Figure 4.21: Adsorption of toluene by foam formulation J with 60 sec. EBRT and influent concentration of 6.95 ppm_v

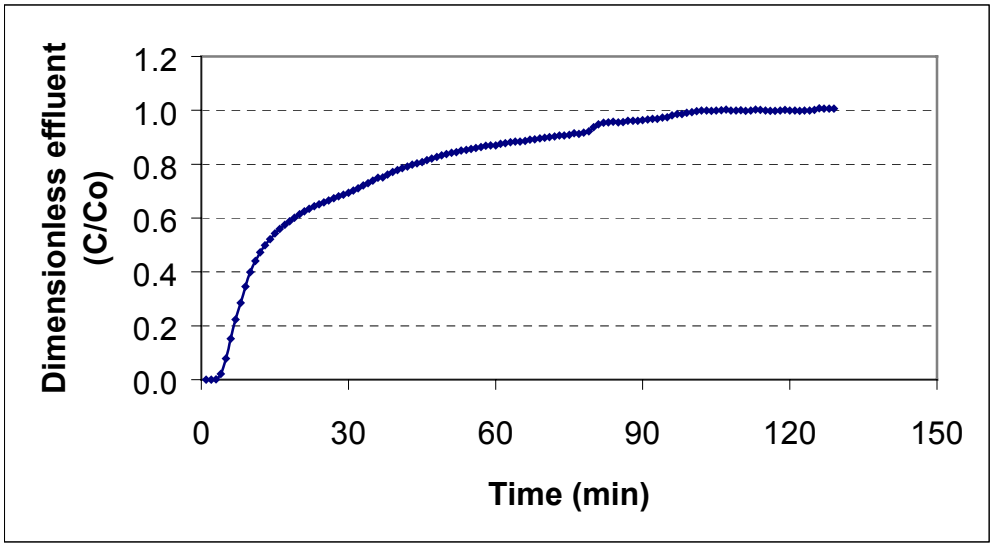

Figure 4.22: Adsorption of toluene by foam formulation J with 20 sec. EBRT and C_o=99.8 ppm_v

Fixed-bed adsorption data for foam formulation M at 6.95 and 99.9 ppm_v of toluene and 20 seconds EBRT are shown in Figure 4.24. The influent toluene masses were 3214 mg and 84.3 mg, the effluent toluene masses were 2660 mg and 54.4 mg, and the total sorbed masses were 554.4 mg and 29.9 mg, respectively. As can be seen from the figure and table, 10% of the influent toluene concentration was observed in the effluent after 4 min and 9 min for influent concentrations of 6.9 ppm_v and 99.8 ppm_v, respectively, with an EBRT of 20 seconds.

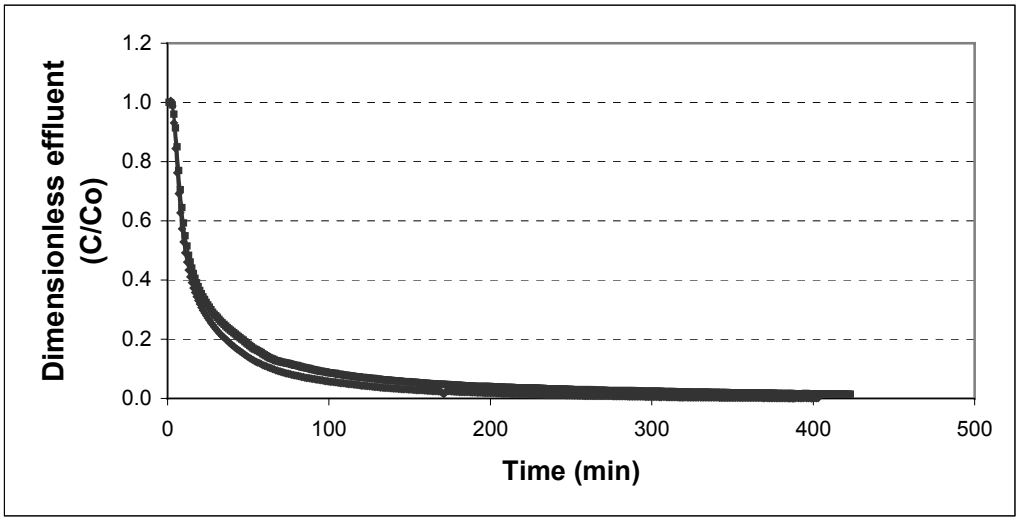

Figure 4.23: Desorption of toluene by foam formulation J with 20 sec. EBRT at 99.8 ppm_v

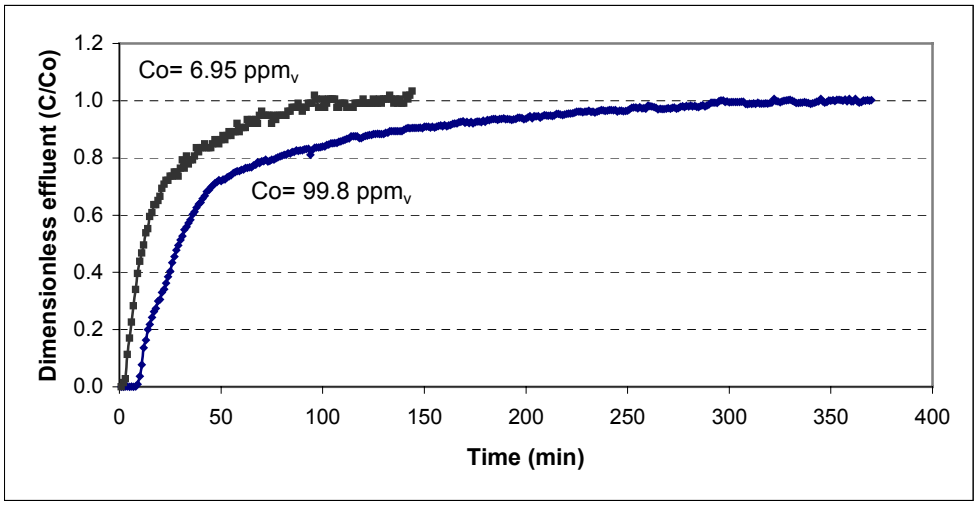

Figure 4.24: Adsorption of toluene by foam formulation M with 20 sec. EBRT

Data for toluene desorption from foam formulation M is shown in Figure 4.25. The total desorbed mass was 27.5 mg, for an influent concentration of 6.95 ppm_v and 20 sec. EBRT, and 596 mg to 99.9 ppm_v and 20 sec. EBRT test. As can be seen from Figure 4.25, the effluent toluene concentration decreased rapidly during the initial

period in a similar way to previously formulations tested. Subsequently, there was a less rapid decrease in the toluene concentration. For example, it took only 192 min and 156 min for the dimensionless effluent concentration to decrease from 1.0 to 0.1 at initial influent concentration of 6.9 ppm_v and 99.86 ppm_v, respectively. And it took additional 169 and 422 min to reach 0.05 for an EBRT of 20. The total mass sorbed and desorbed for 6.9 ppm_v was similar; there was only a 5.6% of variability. For an influent concentration of 99.9 ppm_v there was a difference of a 6.8% between the mass sorbed and desorbed.

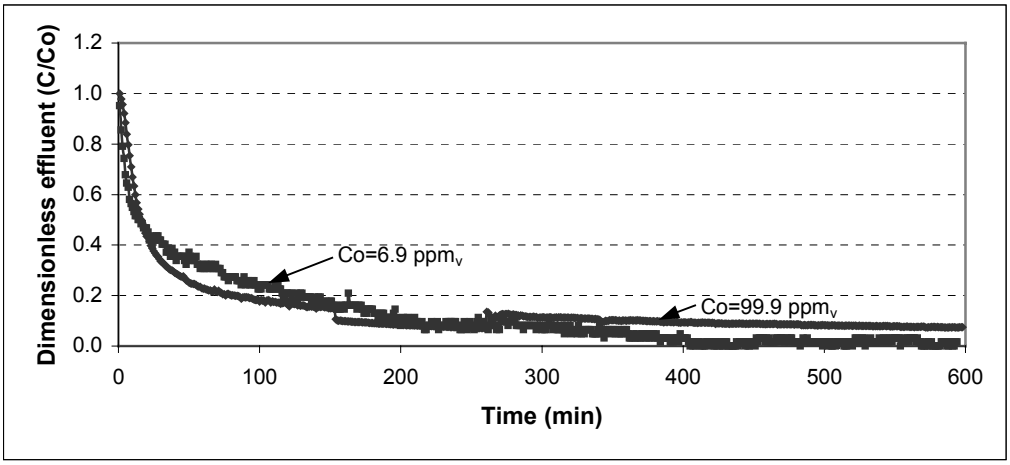

Figure 4.25: Desorption of toluene by foam formulation M with 20 sec. EBRT

Honeywell foam was also tested in fixed bed adsorption and desorption experiments with toluene as the influent VOC. Figure 4.26 shows data collected from adsorption of toluene at 20 sec. EBRT. Table 4.9 summarizes the sample conditions and experimental results. As can be seen from Figure 4.26, 10% of the influent toluene concentration was observed in the effluent after 108 min and 22 when the initial concentration was 100 ppm_v and 500 ppm_v, respectively.

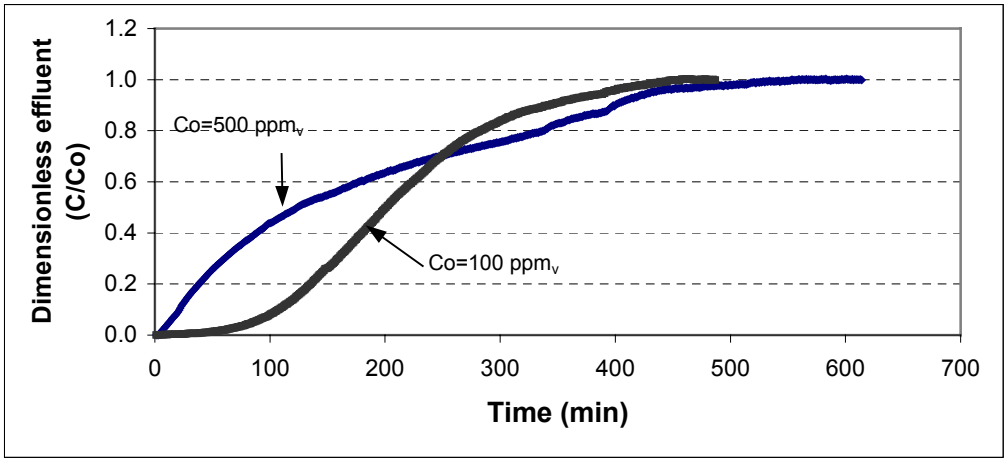

Figure 4.26: Adsorption of toluene by Honeywell foam with 20 sec. EBRT

Table 4.9: Adsorption test conditions and results for Honeywell foam

EBRT (sec.)	Gas Concentration (ppm_v)	Total Influent Mass (mg)	Mass in Effluent (mg)	Total Mass Adsorbed (mg)	Mass Adsorbed * (mg)
20	100	4046	1786	2260	2259.8
20	100	4747	2438	2309	2308.8
20	500	272260	19287	8272	8271.3

*Calculated using Henry's law and the mass of the water to quantify the mass of toluene absorbed in the water.

Figure 4.27 presents desorption data for Honeywell foam with 20 sec. EBRT and initial toluene concentrations of 100 ppm_v and 500 ppm_v. Table 4.10 summarizes test conditions and results. As can be seen from the figure, the effluent toluene concentration decreased rapidly during the initial period following removal of toluene from the influent gas stream. Subsequently, there was a less rapid decrease in the toluene concentration. For example, it took 528 min and 233 min for the dimensionless effluent concentration to decrease from 1.0 to 0.2, while it took additional 420 and 112 min to decrease to 0.1 for an EBRT of 20 and initial toluene concentration of 100 ppm_v and 500 ppm_v, respectively. An additional 250 min was necessary to decrease the dimensionless effluent concentration to 0.05 for the test with an initial toluene concentration of 500 ppm_v.

To compare the dynamic adsorption and desorption behavior of the various foam formulations tested by fixed-bed studies, Figures 4.28 and 4.29 show the adsorption and desorption of toluene for all the formulations tested at 20 seconds EBRT and influent concentration of approximately 100 ppm_v (actual influent concentrations are shown in previous tables).

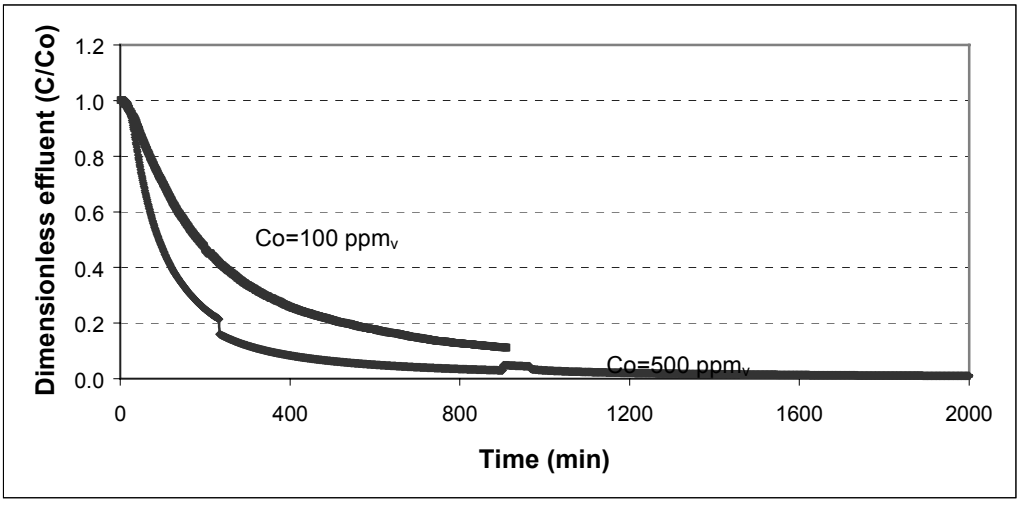

Figure 4.27: Desorption of toluene by Honeywell foam with 20 sec. EBRT

Table 4.10: Desorption test conditions and results for Honeywell foam

EBRT (sec.)	Initial Gas Concentration (ppm_v)	Total Mass Desorbed (mg)
20	100	15.6
20	500	234.7

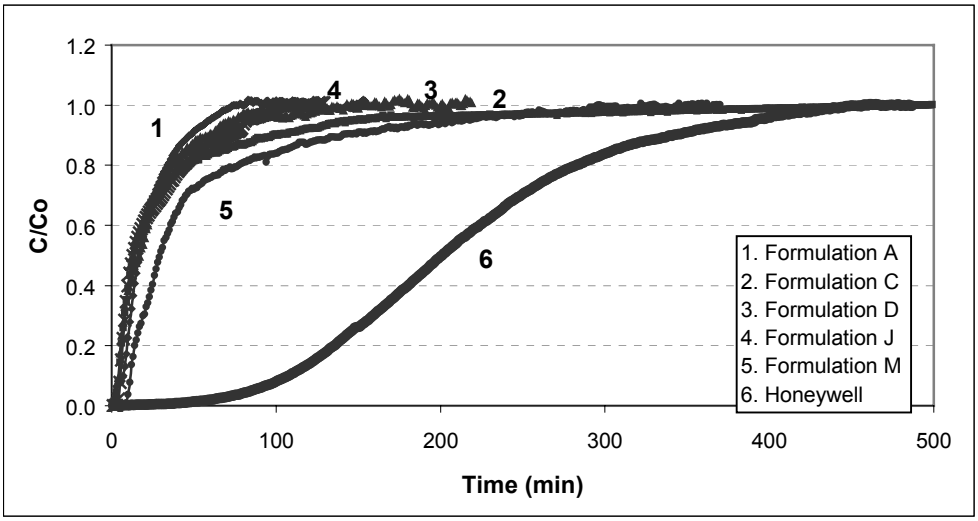

Figure 4.28: Adsorption comparison for toluene with 20 sec. EBRT and approximately 100 ppm_v

Freundlich isotherm parameters were calculated using data collected using PID measurements from fixed-bed adsorption and desorption and GC (at equilibrium concentrations) analysis of batch sorption experiments. Figure 4.30 depicts Freundlich adsorption isotherms for toluene all foam formulations tested. The Freundlich constants (K_f and 1/n) for each foam formulation and contaminant type were calculated along with the correlation coefficients (R^2 values). Table 4.11 summarizes the Freundlich parameters for foam formulations A, C, D, M, and Honeywell. The K_f values for formulations A, C, and D increased as the PAC content of the media increased from 0 to 26.8% by mass while the parameter 1/n decreased slightly. Honeywell foam presented the highest K_f coefficient (one order of magnitude larger), but the slope of this line was appreciably different from the media tested.

The slopes of the Freundlich adsorption equations for the various foam formulations are not parallel, so a general comparison of parameters is difficult; however, the sorption capacity of the various formulations can be easily compared for a specific equilibrium concentration. For this reason, an equilibrium concentration of 1.0 mg/L was selected as a basis of comparison, and the (x/m) Freundlich parameter was calculated from isotherm equations for the foam formulations tested. It should be noted that 1.0 mg/L as an equilibrium aqueous-phase concentration is that expected to be in equilibrium with a gas-phase concentration of 0.265 mg/L in gas phase (69.9 ppm_v). Table 4.12 shows the calculated parameter x/m from C_e equal to 1.0 mg/L, with values sorted from highest to lowest. As can be seen from the table, the

Honeywell foam had the highest sorption capacity, with a x/m value nearly ten times higher than the foam with the next highest sorption capacity.

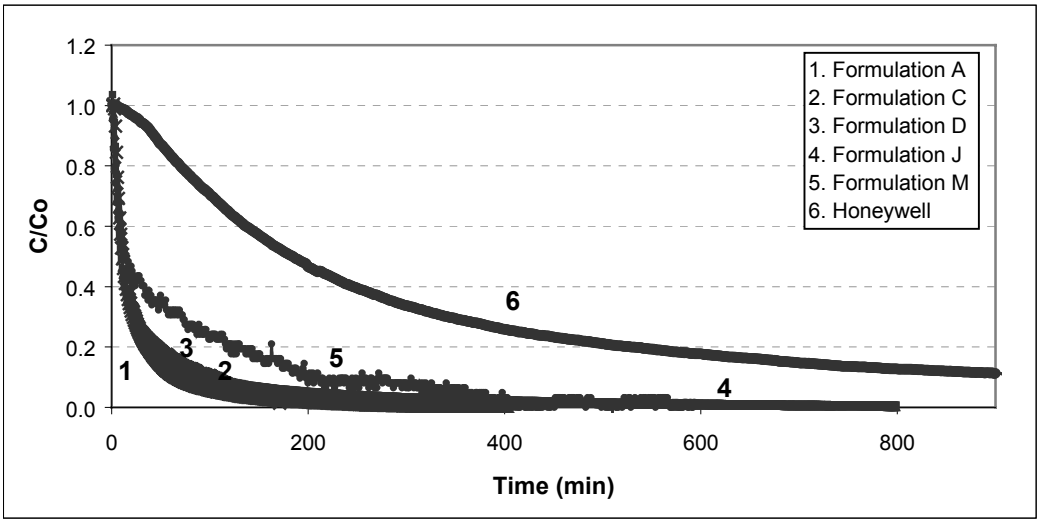

Figure 4.29: Desorption comparison for toluene 20 sec. EBRT

The mass of adsorbate adsorbed per unit volume of absorbent (x/v) was calculated based on Freundlich isotherm parameters (x/m) obtained previously. This new parameter describes how much toluene can be accumulated per unit volume of packing medium based on its density. This term was calculated as an additional basis of comparison because the densities of the various media tested varied appreciably (see Table 4.4). The (x/v) term was obtained multiplying each (x/m) by the dry density of foam. Results are summarized in the Table 4.13. The mass of toluene sorbed per unit volume of packing medium (x/v) was more than eight times higher for the Honeywell packing media than for the material with the next highest (x/v), foam formulation M.

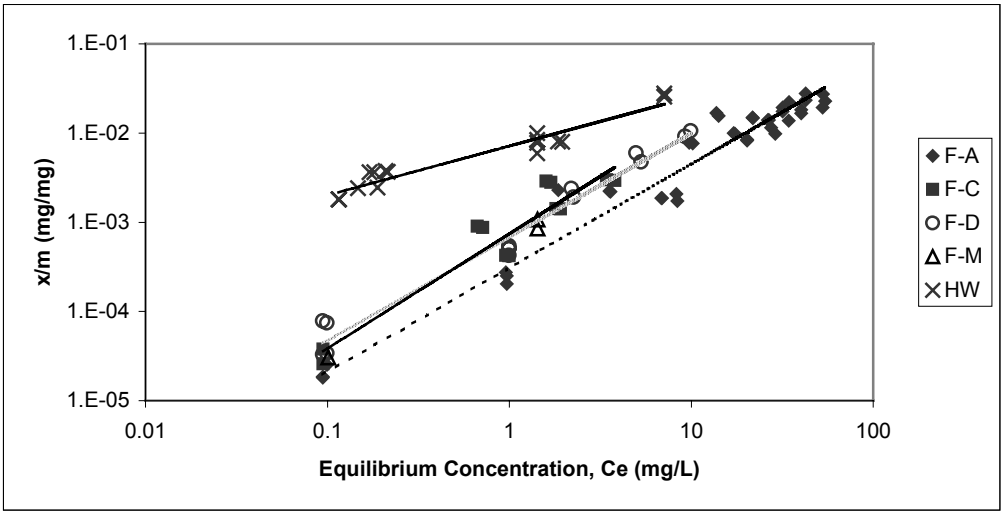

Figure 4.30: Freundlich isotherms adsorption for toluene sorption to various media

Table 4.11: Summary of Freundlich parameters for toluene sorption to various media

Foam formulation	K_f	1/n	R^2
A	0.00031	1.16	0.903
C	0.00068	1.29	0.896
D	0.00074	1.16	0.974
M	0.00060	1.30	0.970
Honeywell	0.00716	0.53	0.929

Table 4.12: Calculated (x/m) Freundlich isotherm parameter at 1.0 mg/L liquid phase for toluene

Foam Formulation	Calculated x/m (mg/mg)
Honeywell	0.00720
D	0.00074
C	0.00068
M	0.00060
A	0.00031

Table 4.13: Mass of toluene sorbed per unit volume of packing media at an equilibrium concentration of 1.0 mg/L

Foam Formulation	x/m at Ce=1 (mg/L)	Dry Density (mg/mL)	x/v (mg/mL)
A	0.00031	82.4	0.02553
C	0.00068	89.3	0.06070
D	0.00074	94.9	0.07020
M	0.00060	118.8	0.07126
Honeywell	0.00720	83.3	0.600

Chatzopoulos (1994) and Chatzopoulos and Varma (1995) conducted batch sorption experiments using Calgon F-300, the same type of PAC used in the studies to manufacture foam formulations A to E described herein. Freundlich isotherm parameters for PAC, reported by those researchers, were used to evaluate the amount of PAC sorption capacity retained during the manufacture process. A "theoretical value" of (x/m) was calculated for each formulation at a equilibrium concentration of 1.0 mg/L of toluene based on the final percent of PAC by mass of each formulation, and (x/x) Freundlich parameters for formulation A (no PAC) and PAC alone assuming that all the PAC sorption capacity was retained during the manufacture process. Thus, the theoretical (x/m) was calculated as the fraction by mass of PAC of the formulations times the (x/m) value of only PAC plus one minus the fraction of PAC (the fraction of foam) times the (x/m) value of Formulation A. Another parameter named "Percent of theoretical (x/m)" was calculated to compare the experimental determined adsorption capacity of foam formulations tested with that expected assuming all of the PAC's sorption capacity retained during manufacture. The "Percent of theoretical (x/m)" was calculated as experimental (x/m) divided by theoretical (x/m) times 100%. Table 4.14 shows all the parameters calculated for foam formulations C and D. Foam formulations C and D had experimentally determined x/m values only 3.5% and 2.8%, respectively, of the value expected if all of the PAC sorption capacity was retained during the manufacture process. Clearly, the majority of the PAC's sorption capacity was lost.

Table 4.14: Comparison of PAC sorption capacity with values predicted assuming no loss of sorption capacity during manufacture.

Foam Formulation	x/m at Ce=1 mg/L (mg/mg)	Theoretical * x/m (mg/mg)	Percent of Theoretical x/m Achieved
A	0.00031	0.00031	100%
C	0.00068	0.01935	3.5%
D	0.00074	0.02689	2.8%
PAC	0.09950	0.09950	100%

* Assumes all of the activated carbon sorption capacity was retained during the manufacturing process.

Moe and Irvine (2000) reported similar results. Adsorption capacity of polyurethane foam containing PAC increased as the mass of PAC increase in the composite material. However, sorption capacity of foam formulation manufactured in the lab were quite low compared with the theoretical capacity (assuming that all the PAC fraction maintaining all of its sorption throughout the manufacture process.). There are several possible explanations for this phenomenon. First, during the manufacture process many of the adsorptive sites of the activated carbon may become occupied by any of components of the foam matrix (e.g. surfactant, polymer, or cross linking agents.) Data showing low surfactant recovery during the rinsing process

supports this hypothesis. Second, during manufacture, PAC becomes part of the polyurethane matrix, and PAC completely surrounded by the polyurethane may be physically blocked from contact by the toluene. Regardless of the exact mechanism, attempts to temporarily block the active sites with water (formulation F to K and M) or toluene (formulations L1 and L2) were largely ineffective in increasing the sorption capacity of the foam. Likewise, increasing the rinse water temperature in an attempt to desorb residual surfactant or other compounds that might occupy active sites in the PAC were relatively ineffective in increasing the media sorption capacity.

4.5 Conclusions

Based on the results presented in this chapter, Honeywell foam cubes and cylinders of polyurethane foam formulation D were selected for more detailed evaluation as described in Chapters 5 and 6. Honeywell foam exhibited superior performance in terms of low head loss and high toluene sorption capacity in comparison to the other media under the conditions tested. Low head loss and high porosity reduce the risk of medium clogging when used in biofiltration, and high toluene adsorption capacity is a necessary characteristic for implementation of sequencing batch operation. Foam formulation D, which had second highest sorption capacity (on a mass basis) of the materials for which sorption capacity was determined, while at the same time having low head loss (see Figure 4.9) was also selected. Although polyurethane foam formulation M, which used Westvaco PAC, had higher adsorption capacity than did foam formulation D (on a volumetric basis), the material's wet density was comparatively high and it exhibited much higher head loss (see Figure 4.10). For these reasons, it was not selected for further evaluation.

CHAPTER 5 MATERIALS AND METHOD FOR DETAILED EVALUATION

Two types of foam media were selected (from the initial fifteen types of packing tested) for a more a detailed evaluation. Foam formulation D and Honeywell foam were selected based on results presented in chapter 4. Foam formulation D was manufactured and rinsed as described in section 3.1, and Honeywell polyurethane foam cubes were prepared as described in section 3.1.4.

For each of the two packing media, experiments were conducted to determine the equilibrium sorption capacity for toluene, p-xylene, methyl ethyl ketone, and methyl isobutyl ketone batch for single component solutions (i.e., each compound tested separately) and multicomponent solutions (all compounds present). Dynamic fixed-bed experiments were conducted using toluene and methyl ethyl ketone, and bed depth service time analysis was conducted. Finally, experiments were conducted to assess the media resistance to chemical degradation. Specific methods for each of these experiments are described in the following sections.

5.1 Equilibrium Isotherm Adsorption

Batch isotherm experiments were used to quantify sorption characteristics for toluene, p-xylene, methyl ethyl ketone, and 4-methyl-2-pentanone on to polyurethane/PAC foam. Batch isotherm experiments were conducted initially using single component solutions (i.e., each compound was tested separately). Different masses of foam were placed into amber glass bottles, filled with tested compound solution, covered with teflon-silicone septa caps, and placed in a tumbler for 48 hours. The mass of foam in each bottle ranged from 0 to 10 g, and the initial VOC concentration ranged from 50 to 500 mg/L. After 48 hours, aqueous samples were removed and the VOC concentration in the bulk liquid was measured. Freundlich isotherm parameters were used to describe the adsorption of each compound and media combination tested.

VOC analysis was conducted using a gas chromatograph equipped with a purge and trap using the same equipment and method described in section 3.3.5. Although the retention times are all very similar, peaks separation were not necessary because each compound was tested individually.

A competitive adsorption isotherm test was conducted using a combination of compounds tested previously to assess the potential for competitive adsorption. Solutions containing two different initial concentrations were made with the composition show in Table 5.1.

Table 5.1: Target aqueous-phase concentration of individual compounds for a mix adsorption test

Compound	High Concentration (mg/L)	Low Concentration (mg/L)
p-Xylene	158.9	79.5
Toluene	140.5	70.2
Methyl ethyl ketone	405.5	203.3
Methyl isobutyl ketone	1088.7	547.5

The purge, trap, and GC equipment as well as the method used for separation and quantification of compounds in the multicomponent solutions were identical to those described in section 3.3.5 except for the GC temperature program. For analysis of the multicomponent solution, the oven temperature was set at 40 ^{o}C for 4 minutes, then increased at a rate of 10 degree per minute for 16 minutes. The retention times for methyl ethyl ketone, 4-methyl-2-pentanone, toluene, and p-xylene were 10.44 minutes, 14.77 minutes, 15.09 minutes, and 17.76 minutes, respectively.

5.2 Bed-Depth Service Time

A BDST test was conducted using Honeywell foam and foam formulation D using two glass columns (described in section 3.2.7) connected in series. A schematic diagram of the apparatus is depicted in Figure 5.1.

Approximately 20 L of Honeywell foam were cut in to smaller cubes of 1.25 cm per side and placed to dry over night in a laboratory oven at 65 ^{o}C. Metal support plates were installed in the bottom of the first and third glass sections to hold equal masses of foam cubes. A total of 296 g of foam cubes were used to fill the 4 sections of each glass column giving a total bed depth of 95 cm for each column and a total mass of 592 g of foam (total of both column combined). Foam cubes were slightly compressed to adjust them to the desired bed depth. Each column was filled with deionized water to wet the foam cubes, and then it was drained by gravity. The masses of the wet foam were later measured to determine the moisture content of the medium during the subsequent adsorption test.

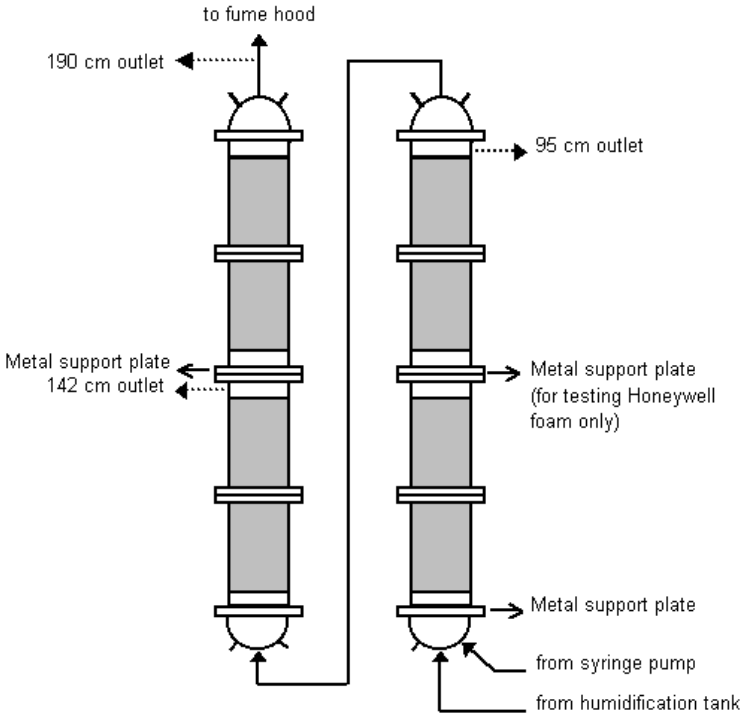

Figure 5.1: Column apparatus used to conduct bed-depth service time experiments

On the other hand, 10 foam formulation D cylinders were used to pack two glass columns exactly the same as those used for Honeywell foam. The 10 cylinders provided a total packing depth of 190 cm (total of both columns). For BDST tests for both foam types, the specific compound tested was delivered by syringe pump through a glass gas-tight syringe into the air stream in the same way used for previously described fixed-bed adsorption and desorption experiments (see section 3.2.2).

For the BDST experiments, contaminant concentration was measured as a function of time at three different heights along the biofilter columns (95, 142, and 190 cm). Breakthrough was defined as the time when a specified amount of influent contaminant concentration (10 and 90 percent) was detected in the effluent. The experiment was repeated for two different compounds (toluene and methyl ethyl ketone). The characteristics of this test are summarized in Table 5.2. For the BDST test, the gas flow was 3.65 L/min. This corresponds to an EBRT of 240 seconds for a column of 190 cm in height and 76.98 cm^2 in cross-sectional area.

Table 5.2: BDST test for Honeywell foam and formulation D

Compound	Gas Concentration (mg/L)	Gas Concentration (ppm_v)	Gas Flow Rate (L/min)	Bed Depth (cm)
Toluene	1.90	496.4	3.65	190
				147
				95
MEK	1.48	500.7	3.65	190
				147
				95

5.3 Chemical Resistance Test

Both types of polyurethane foam were tested for chemical resistance. Approximately 5 g of pre-weighed foam cubes were placed into 260 mL amber glass bottles, which were then totally filled with different solutions, covered with teflon-silicone septa caps and placed in a tumbler for 48 hours. At the end of 48 hours, the foam cubes were removed from the bottles. A visual inspection was made for obvious changes in the foam properties, and then the cubes were placed in a fume-hood over night. Then, the foam cubes from acid and basic solution tests were rinsed several times with deionized water. Then, the foam cubes were placed for at least 24 hours in a laboratory oven at 65 ^oC. Finally, the mass of the foam cubes was weighed to determine if any variation occurred. Five different solutions were used for this test; pure toluene and methyl ethyl ketone from Fisher Scientific (Fair Lawn, NJ); bleach from Clorox (Oakland, CA); sodium hydroxide and hydrochloric acid both at 0.25 molar concentration (Fisher Scientific).

CHAPTER 6 RESULTS AND DISCUSSION FOR DETAILED EVALUATION

6.1 Equilibrium Isotherm Adsorption

6.1.1 Honeywell foam

Figure 6.1 depicts results of batch isotherm experiments that tested each compound separately (i.e., single component solutions) using Honeywell foam. Results are presented using the same scale for comparison purposes. All individual analyses are presented in Appendix 4.

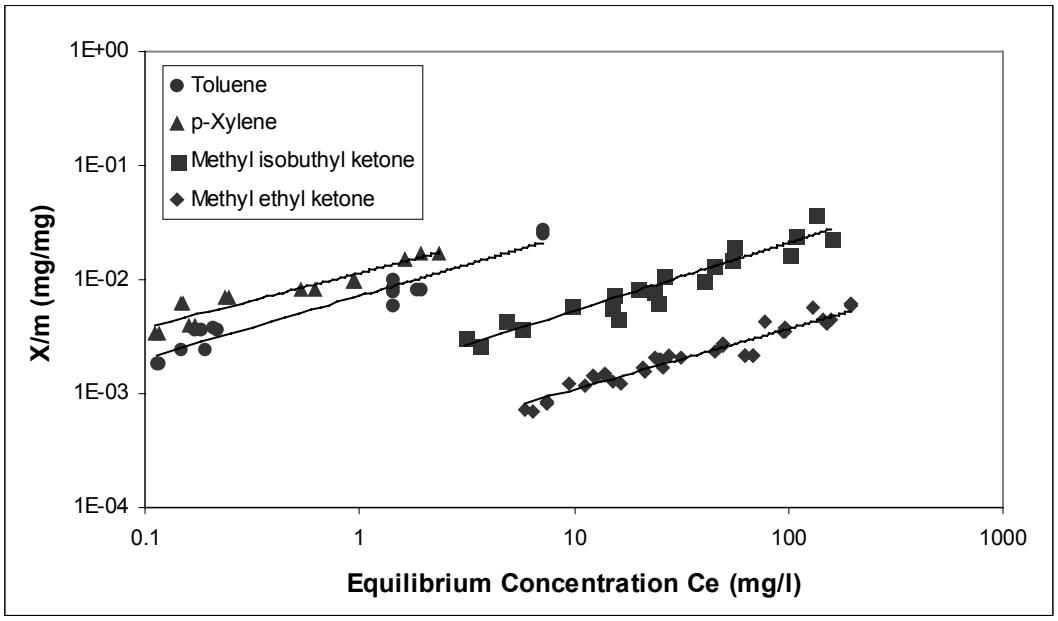

Figure 6.1: Freundlich isotherm for Honeywell foam. Compounds were tested separately in single component solutions

Table 6.1: Freundlich constants for adsorption of single component solution to Honeywell foam

Compound	K_f	$^1/n$	R^2
p-Xylene	0.0114	0.482	0.90
Toluene	0.0072	0.551	0.93
Methyl ethyl ketone	0.0014	0.597	0.92
Methyl isobutyl ketone	0.00032	0.534	0.92

Freundlich constants (K_f and $^1/n$) for each compound were calculated along with the correlation factor (R^2 value). Results are summarized in Table 6.1. In all cases, the R^2 value was greater then 0.9 indicating that the Freundlich isotherm adequately describes the experimental data. As can be clearly seen from Figure 6.1 and data in Table 6.1, p-xylene had a higher affinity for the media than did toluene,

MEK, or MIBK. Aromatic compounds presented a higher adsorptive affinity for the foam than did ketones.

A comparison of Freundlich parameters reveals that p-xylene had a higher affinity for the media than did other compounds. The slope of the line changed for all compounds tested indicating competitive adsorption. There was some similarity between the slopes of the lines for the aromatic compounds and similarity between the lines for the ketones.

6.1.2 Formulation D

Results of batch isotherm experiments for sorption of single component solution of toluene and methyl ethyl ketone to foam Formulation D are shown in Figure 6.3. Table 6.3 summarizes the corresponding Freundlich parameters and correlation coefficients. All individual analyses are presented in Appendix 5.

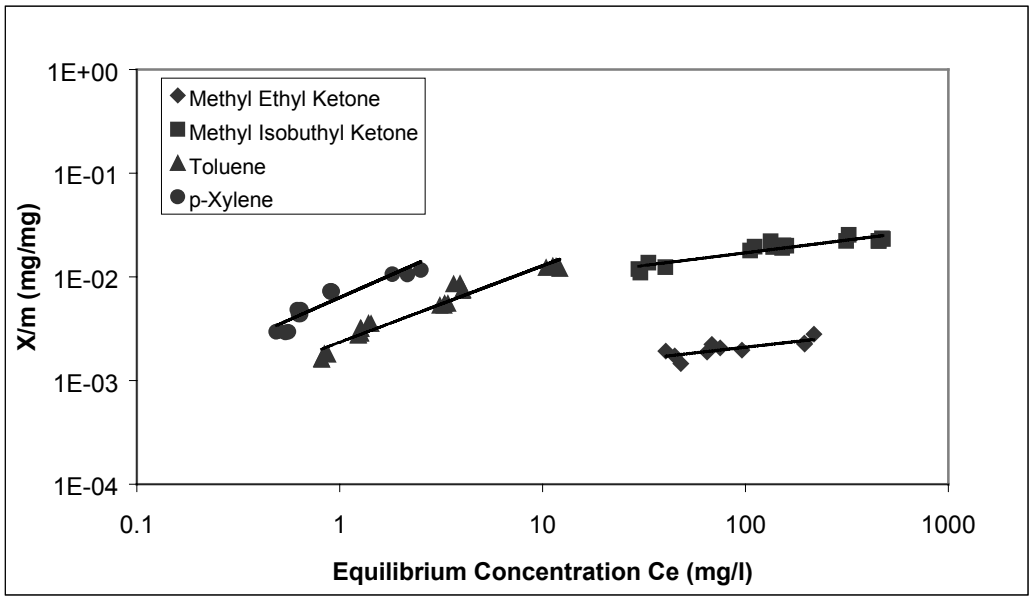

Figure 6.2: Competitive adsorption test for Honeywell. Compounds were tested in multicomponent solutions.

Table 6.2: Freundlich coefficient constants for Honeywell foam competitive adsorption experiments

Compound	K_f	$^1/n$	R^2
p-Xylene	0.0063	0.857	0.89
Toluene	0.0023	0.798	0.95
Methyl ethyl ketone	0.0055	0.245	0.88
Methyl isobutyl ketone	0.00083	0.221	0.72

Based on the Freundlich parameters, toluene presented higher adsorption affinity for foam formulation D than did MEK. In both cases, the K_f values obtained for foam Formulation D were more than an order of magnitude smaller than those found for Honeywell foam.

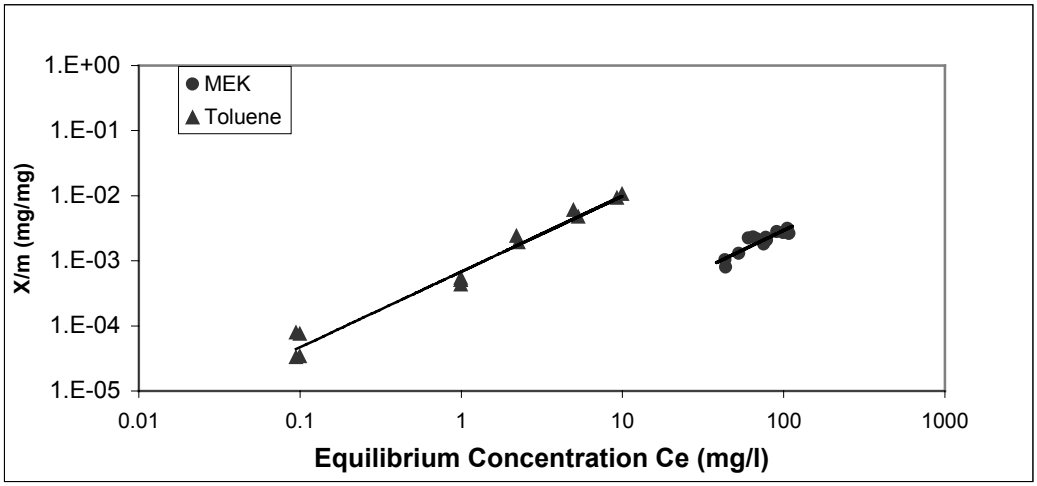

Figure 6.3: Freundlich isotherm for foam formulation D. Compounds were tested separately in single component solutions.

Table 6.3: Freundlich constants for adsorption of single component solution to foam Formulation D

Compound	K_f	$^1/n$	R^2
Toluene	0.00068	1.162	0.97
Methyl ethyl ketone	0.000051	1.191	0.82

6.2 Bed-depth Service Time

6.2.1 Honeywell foam

Figure 6.4 shows the breakthrough of methyl ethyl ketone at bed depths of 95 cm, 142 cm and 190 cm for columns containing Honeywell foam loaded with a gas stream containing 500 ppm_v as influent concentration at a flow rate of 3.65 L/min.

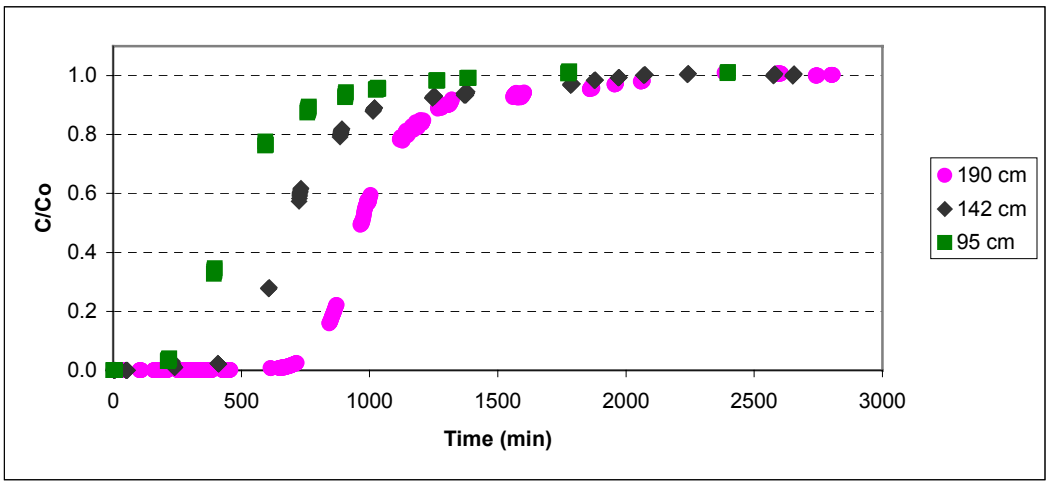

Figure 6.4: Breakthrough of MEK in Honeywell foam with inlet concentration 500 ppm_v and gas flow rate of 3.65 L/min

The breakthrough graphs depicted in Figure 6.4 were used to predict BDST and obtain Bohart-Adams equation parameters. The time values corresponding to 10 and 90% breakthrough were plotted as a function of bed depth, and the resulting graph is depicted in Figure 6.5. The slope of the BDST is equal to the reciprocal of the velocity of the adsorption zone, and the X intercept is the critical depth defined as the minimum bed depth required to obtain the desired effluent quality at time zero. In this case, the velocity of the adsorption zone was 0.19 cm/min and the critical bed depth was 42 cm (for 10% breakthrough). The horizontal distance between the 90 and 10% lines in the BDST graphic (calculated by setting y=0 in the respective equations and calculating the distance between the x intercepts) represents the height of the adsorption zone which in this case was approximately 92 cm.

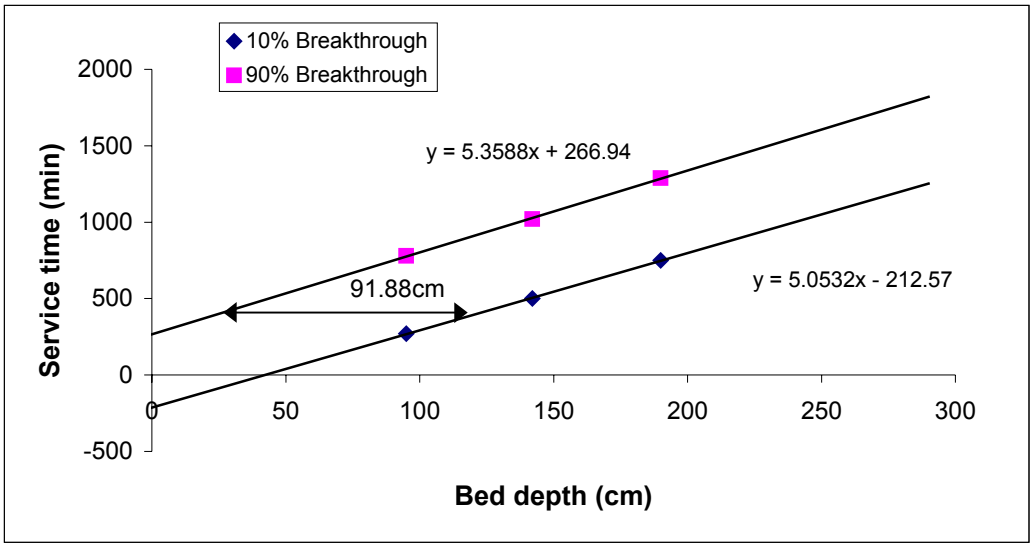

Figure 6.5: BDST for MEK in Honeywell foam with inlet concentration 500 ppm_v and gas flow rate of 3.65 L/min.

Honeywell foam was also tested for BDST with toluene. The test conditions used a gas flow rate of 3.65 L/min and an influent toluene concentration of 499 ppm_v, conditions similar to those used for methyl ethyl ketone. Figure 6.6 shows the breakthrough of toluene at various bed depths for Honeywell foam.

Figure 6.7 shows the BDST graph for toluene on Honeywell foam using results depicted in Figure 6.6. The critical depth, measured as X intercept, was 52 cm, the height of the adsorption zone (horizontal distance between lines) was 132 cm, and the velocity of the adsorption zone was 0.14 cm/min.

Using the appropriate modifying factor to account for changes in the flow rate (equation 2.5, see section 2.8), the Bohart-Adams equation determined for toluene at flow rate of 3.65 L/min (see Figure 6.7) was modified to predict breakthrough behavior for a gas with the same toluene concentration but with a flow rate of 21.9 L/min. The BDST predicted using this method is graphically represented in Figure 6.8.

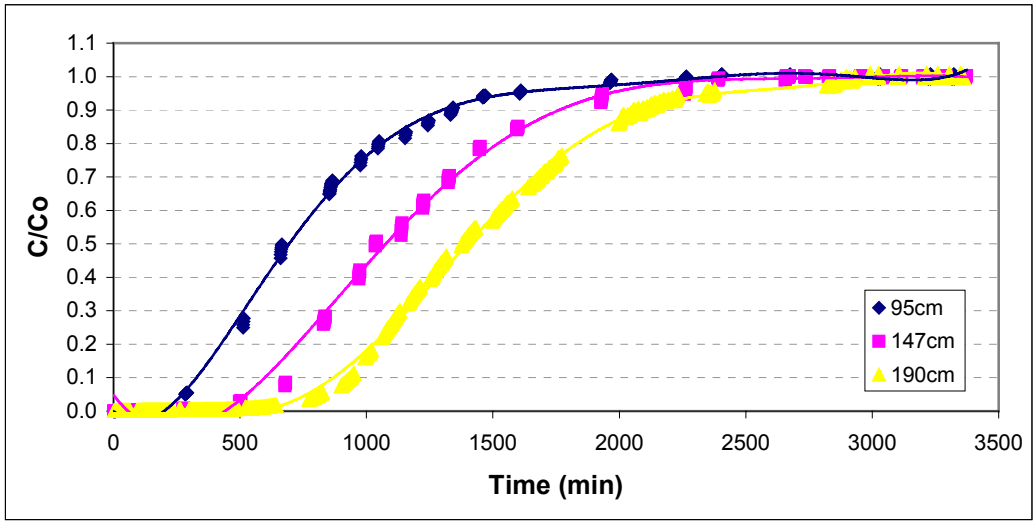

Figure 6.6: Breakthrough for toluene and Honeywell foam with inlet concentration of 499 ppm_v and gas flow rate of 3.65 L/min

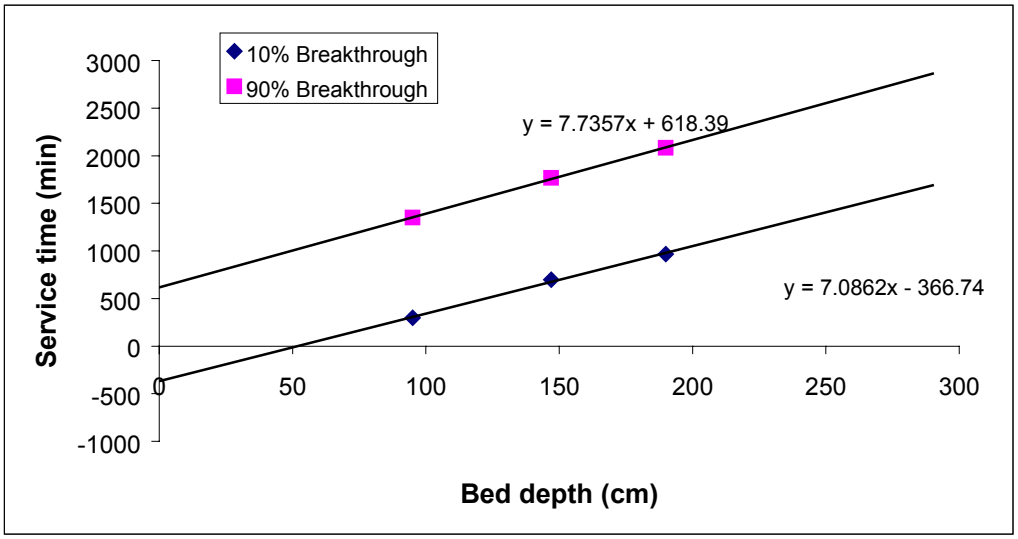

Figure 6.7: BDST for toluene and Honeywell foam with inlet concentration of 499 ppm_v and gas flow rate of 3.65 L/min.

The predicted breakthrough curve for the Honeywell foam is shown in comparison to measured data for a breakthrough determined for a gas flow rate of 21.9 L/min using the same type of foam and the same bed depths. Figure 6.8 shows how the Bohart-Adams model prediction compared to measured data at 90% breakthrough.

A likely explanation for the fact that the predicted data disagreed with measured data is that for the highest flow rate, the horizontal distance between the lines for 10% breakthrough and 90% breakthrough (the height of the adsorption zone) was approximately 800 cm. The 195 cm of total bed depth was insufficient for the test with a flow rate of 21.9 L/min because the total bed height was smaller than the height of the adsorption zone.

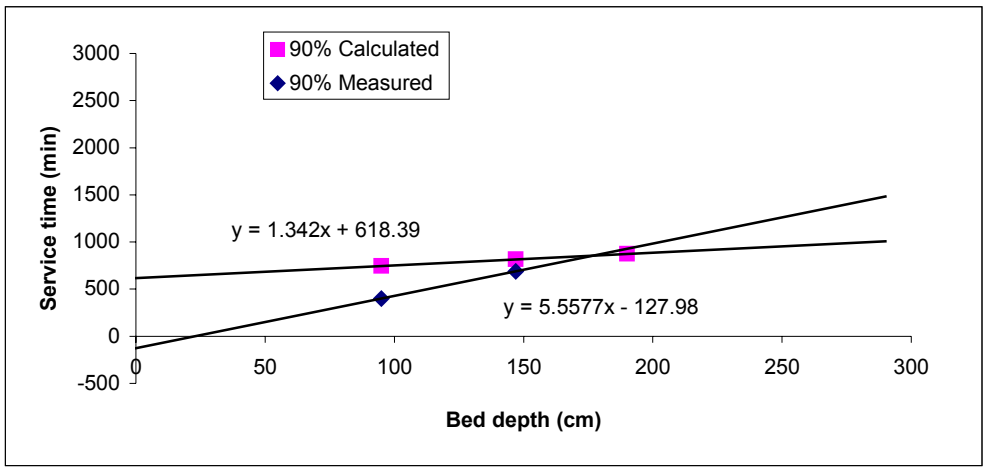

Figure 6.8: Comparison of measured and calculated BDST parameters for Honeywell foam for an influent toluene concentration of 500 ppm_v and gas flow rate of 21.9 L/min

6.2.2 Formulation D

Figure 6.9 shows the breakthrough of methyl ethyl ketone as a function of time for bed depths of 96 cm, 144 cm, and 192 cm for foam formulation D loaded with an influent MEK concentration of 500 ppm_v and a gas flow rate of 3.65 L/min. As can be clearly seen from the figure, foam formulation D exhibited a different adsorptive behavior compared to the Honeywell foam. The initial breakthrough was faster than that observed for experiments using Honeywell foam, and an appreciable "tailing effect" was observed as C/C_o approached a value of 1.0. Using data presented in Figure 6.9, a BDST plot was made for toluene and foam formulation D. Figure 6.10 shows BDST for methyl ethyl ketone for foam formulation D.

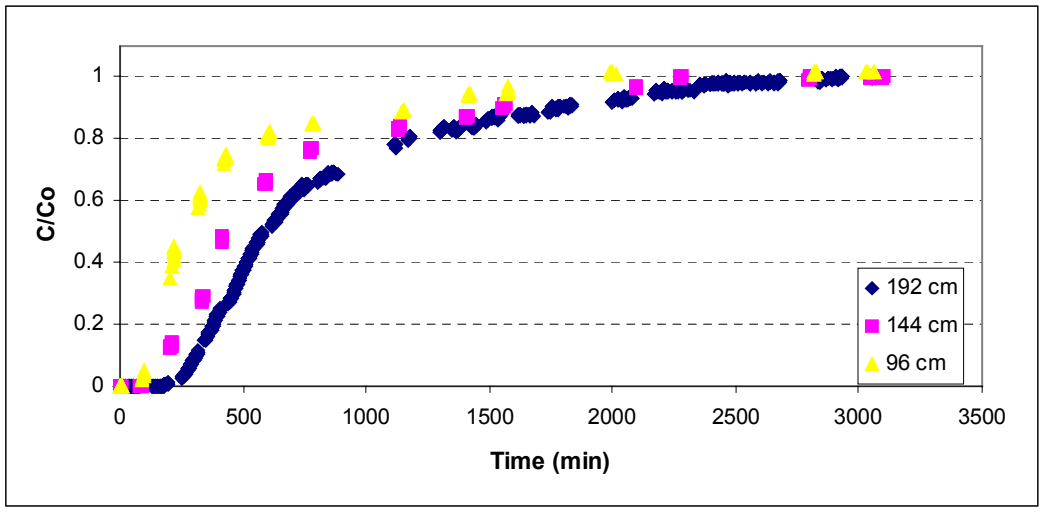

Figure 6.9: Breakthrough adsorption for MEK in foam formulation D with inlet concentration 500 ppm_v and flow rate of 3.65 L/min

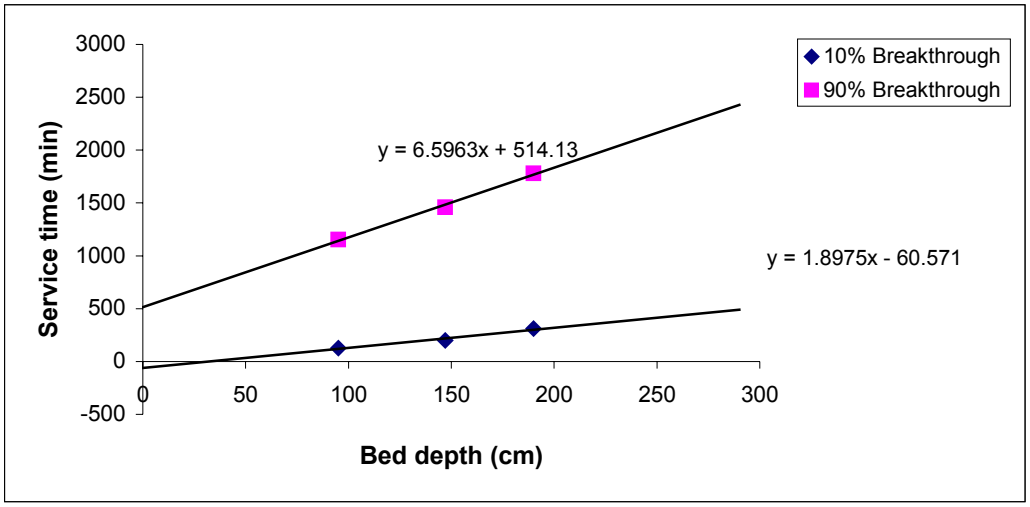

Figure 6.10: BDST for methyl ethyl ketone and foam formulation D with inlet concentration 500 ppm_v and gas flow rate of 3.65 L/min

As clearly shown in Figure 6.10, the 10 and 90 % breakthrough lines are not parallel in this case. This provides a clear indication that the height of the absorption zone is greater than the total bed depth used in this experiment.

Results indicate that the Honeywell foam has more favorable adsorption kinetics than foam formulation D because the former foam had a shorter adsorption zone height and required a smaller bed depth in order to achieve a specified removal efficiency. Similar results (data not shown) were found with foam formulation D and toluene where fast breakthrough was established at the beginning of the test.

One potential explanation for this phenomenon is differences in the polyurethane/PAC matrix. The carbon in foam formulation D was mixed with Hypol in the preparation process, so the carbon is an integral part of the foam matrix. On the other hand, the Honeywell packing medium has carbon coated to the polyurethane foam after preparation, and consequently, the carbon is at the surface of the foam. In foam formulation D, the initial fast breakthrough may be due to the fact that activated carbon near the surface of the polyurethane foam/activated carbon matrix became saturated rapidly, and the tailing fact is caused by gradual diffusion of the VOC to carbon located further from the surface.

6.3 Chemical Resistance Test

Visual and quantitative measurements were made after immersion of foam pieces in the chemical test agents. The percent recovery was calculated as one minus the difference between initial and final mass divided by the initial mass times 100%. Table 6.5 summarizes the data collected for chemical resistance.

Among the five chemical agents tested, the only one that had a very obviously damaging effect on both types of foam media was Clorox bleach. The other chemicals tested did not cause obvious visible effects; however, the percent recovery of those ranged from approximately 92 to 100%. Further testing may be necessary to ascertain for the solvents (MEK and toluene) damaged the foam media.

Table 6.4: Results of chemical resistance test

Constituent	HONEYWELL FOAM		FOAM FORMULATION D	
	Visible Effect	Recovery	Visible Effect	Recovery
MEK	None	91.9%	None	98.5%
Toluene	None	92.7%	None	98.5%
Acid solution	None	99.8%	None	97.8%
Base solution	None	97.6%	None	96.3%
Clorox bleach	Foam dissolved, black liquid	ND	Foam dissolved, black liquid	ND

ND: not determined

It is important to know the resistance of polyurethane foam against the chemical agents tested for different reasons. MEK and toluene were tested because they are two VOCs present in paint spray booth off-gases discharges, and a biofilter packing medium that is chemically degraded by contaminants would face obvious limitations in use. The acid solution and basic solution were tested because it is known that biodegradation of many compounds produces acid solutions. To neutralize acidic solutions, basic solutions or buffering agents may be added. Clorox bleach was tested because in recent years the addition of NaOCl has been proposed as a method for removing excess biomass accumulation from biofilters (Cox and Deshusses, 2001). Use of such a biomass removal strategy would not be possible with either of the media tested in these experiments because of the obvious damage caused by the chlorine bleach solution.

6.4 Discussion and Conclusions

For applications involving use of the types of polyurethane foam based packing media described herein in conjunction with sequencing batch operation of biofilters treating gas-phase contaminants (see section 2.5), BDST can be used to determine the length of the FEED period assuming no biodegradation takes place during FEED. While this assumption would obviously not be the case for a real biofilter application, it is useful in that it allows one to calculate the minimum FEED period length that could be used. The actual length of FEED that could be used would be greater because the contaminant removal mechanism would be both abiotic sorption and biotransformation. With the BDST correlation, for a specified influent concentration and flow rate, the maximum length of the FEED period which could be used while ensuring specified contaminant removal efficiency in a system with no biodegradation can be calculated for a specified bed depth. Alternately, the necessary bed depth of packing media can be calculate for a given FEED period duration, contaminant concentration, and flow rate.

For example, with the Honeywell foam medium, the BDST equation that describes bed depth versus service time for 10% toluene breakthrough (see Figure 6.7) can be used. For a biofilter containing 100 cm depth of Honeywell packing material receiving an influent toluene concentration of 500 ppm_v at a surface loading rate of 28.4 $m^3/m^2/hr$ (same surface loading rate as the condition tested for data depicted in Figures 6.6 and 6.7), the column could be operated for 306 minutes before 10% contaminant breakthrough would be reached assuming that no biodegradation takes

place. Likewise, a biofilter containing 150 cm depth of Honeywell packing material receiving an influent toluene concentration of 500 ppm_v at a surface loading rate of 28.4 $m^3/m^2/hr$ could be operated for 696 minutes before 10% contaminant breakthrough would be reached (again, assuming that no biodegradation takes place). The same approach could be used for MEK using the corresponding equation that describes 10% breakthrough.

The BDST equation can be used to calculate the height of the adsorption zone for other flow rate by multiplying the original slope by the ratio of the original and new flow rate. Also, the BDST equation can be modified for other influent concentrations to predict the height of the adsorption zone under other test conditions. Examples of this can be found in Tables 6.6 and 6.7 which summarize the predicted height and velocity of the adsorption zone when the influent concentration and flow rate are modified for MEK and toluene respectively, for Honeywell foam. For the calculated values in the table, the allowable effluent concentration was assumed to be 10% of the influent concentration for comparison purposes. The height of the adsorption zone and the velocity of the adsorption zone (or the time to reach a special breakthrough concentration for a column of fixed height) could be calculated assuming other effluent limits by using equation 2.6. In the data presented in the tables, calculations were based on a column with a cross section area of 77 cm^2 (the same as that used in laboratory column studies described throughout this thesis); however, the previously described equation can be easily scaled to other cross sectional areas.

Based on the previously presented data and calculated parameters shown in Tables 6.6 and 6.7, it is interesting to note that the height of the adsorption zone for toluene was greater than that for MEK, even though that the equilibrium isotherm adsorption test showed that toluene has higher affinity to be adsorbed by Honeywell foam and the velocity of the adsorption zone for the toluene was slower than for MEK. A possible explanation for this phenomena is that toluene has a higher Henry's law constant, which causes more mass transfer resistance from gas-phase to the liquid-phase when the stream is passing through the packing media, thus resulting in a larger adsorption zone length. According to the calculations, the height of the adsorption zone does not change with the modification of the influent concentration, contrary to the modification of the flow rate.

Because it was determined that competitive adsorption take place when multiple compounds sorb to both types of polyurethane foam media tested, BDST analysis for a single compound cannot be used to predict design parameters for treatment of VOC mixtures. In order to use BDST to predict the performance of multicomponent gas flows, breakthrough curves for the multicomponent mixture should be experimentally determined. BDST analysis could then be applied for design proposes.

As described in section 2.5, in cases where a continuous contaminated gas flow is generated, multiple biofilter units installed in parallel and operated in sequence could be used. In a multiple biofilter system, the length of time for one biofilter to complete REACT and IDLE would be set equal to the total FILL time of all other biofilters in the system. For example, if four hours are needed to bring the PAC to the

desired sorbent loading level during FEED, but eight hours are needed for REACT and IDLE, then the system will require three biofilters (i.e., as the other two biofilters are in FEED [8 hours total (4 hours in each of two reactors)]), the third biofilter would be in REACT and IDLE [8 hours]).

Table 6.5: Predicted height and velocity of the adsorption zone for different concentrations and flow rates of toluene using Honeywell foam for a column with a cross sectional area of 77 cm^2.

CONCENTRATION (ppm_v)	GASS FLOW RATE (L/min)	EBRT for 1m Bed Depth	HEIGHT OF ADSORPTION ZONE (cm)	VELOCITY OF THE ADSORPTION ZONE (cm/min)
20,000	3.67	126	131.69	5.17
	43.88	20	1574.5	61.8
	87.75	10	3148.9	123.6
	175.51	5	6297.9	1.29
5,000	3.67	126	131.69	1.29
	43.88	20	1574.5	15.5
	87.75	10	3148.9	30.9
	175.51	5	6297.9	61.8
1,000	3.67	126	131.69	0.26
	43.88	20	1574.5	3.1
	87.75	10	3148.9	6.2
	175.51	5	6297.9	12.4
500	3.67	126	131.69	0.219
	43.88	20	1574.5	1.55
	87.75	10	3148.9	3.09
	175.51	5	6297.9	6.18
100	3.67	126	131.69	0.026
	43.88	20	1574.5	0.31
	87.75	10	3148.9	0.62
	175.51	5	6297.9	1.24
10	3.67	126	131.69	0.0259
	43.88	20	1574.5	0.031
	87.75	10	3148.9	0.062
	175.51	5	6297.9	0.12

Fixed-bed desorption experiments for Honeywell foam (see Figure 4.27) indicate that the rate of toluene desorption is sufficiently high to make sequencing batch operation a technically feasible option. For the loading condition where 95 cm depth of Honeywell foam packing medium was equilibrated with an influent toluene concentration of 500 ppm_v at a surface loading rate of 28.4 $m^3/m^2/hr$ and then toluene was removed from the column influent, it took approximately 345 minutes for the effluent toluene concentration to decrease to 10% of the initial value. This provides a clear indication that the desorption rate is sufficiently high to prevent a multiple

biofilter system from requiring an inordinately large number of biofilters installed in parallel to function.

Table 6.6: Predicted height and velocity of the adsorption zone for different concentrations and flow rates of MEK using Honeywell foam for a column with a cross sectional area of 77 cm^2.

CONCENTRATION (ppm_v)	GASS FLOW RATE (L/min)	EBRT for 1m Bed Depth	HEIGHT OF ADSORPTION ZONE (cm)	VELOCITY OF THE ADSORPTION ZONE (cm/min)
20,000	3.67	126	91.88	7.46
	43.88	20	1098.5	89.2
	87.75	10	2196.9	178.5
	175.51	5	4393.9	357.0
5,000	3.67	126	91.88	1.87
	43.88	20	1098.5	22.3
	87.75	10	2196.9	44.6
	175.51	5	4393.9	89.2
1,000	3.67	126	91.88	0.37
	43.88	20	1098.5	4.5
	87.75	10	2196.9	8.9
	175.51	5	4393.9	17.8
500	3.67	126	91.88	0.19
	43.88	20	1098.5	2.23
	87.75	10	2196.9	4.46
	175.51	5	4393.9	8.92
100	3.67	126	91.88	0.037
	43.88	20	1098.5	0.45
	87.75	10	2196.9	0.89
	175.51	5	4393.9	1.78
10	3.67	126	91.88	0.0037
	43.88	20	1098.5	0.045
	87.75	10	2196.9	0.089
	175.51	5	4393.9	0.18

Honeywell foam media had the most favorable adsorptive characteristics of the fifteen biofilter media tested. Results reported herein indicate that the Honeywell media contains the properties desirable for biofiltration packing medium, namely, high sorption capacity, favorable sorption kinetics, and low head loss. Use of a new biofilter operation strategy, sequencing batch operation, may be possible with the use of the Honeywell activated carbon coated polyurethane foam medium.

CHAPTER 7 DISCUSSION AND CONCLUSIONS

Experimental results from the laboratory studies described herein demonstrated that polyurethane foam containing activated carbon has the properties desirable for biofilter packing media. In particular, results suggest that such media contain characteristics necessary for implementation of sequencing batch operating strategies for biofilters treating gas-phase contaminants.

All of the formulations tested for head loss exhibited low pressure drop at gas flow rates expected in biofiltration. This was the case both for foam formulation tested as cylinder monoliths (e.g., foam Formulation D) as well as that in the form of cubed packing (i.e., Honeywell foam). The Honeywell foam medium had the lowest head loss even though it was necessary to use metal plates to support the foam cubes in the test columns. The maximum head loss did not exceed 0.1 cm H_20 even for surface loading rates as high as 300 m^3/m^2*hr.

The Freundlich isotherm model proved adequate to describe the adsorption capacity for all foam formulations tested under equilibrium conditions. Because the equations that best described the adsorptive properties of the various foam formulations were not parallel, the sorption capacity of the various formulations was compared at a specific equilibrium concentration of 1.0 mg/L. Under these conditions, the (x/m) Freundlich parameter was calculated from isotherm equations for the foam formulations tested. The Honeywell foam had the highest sorption capacity, with a x/m value nearly ten times higher than the foam with the next highest sorption capacity for all compounds tested.

For foam formulations manufactured in the laboratory, it was also established that adsorption capacity increased as the mass of PAC increase in the composite material. However, sorption capacity of foam formulation manufactured in the lab was quite low compared with that expected if the activated carbon retained its sorption capacity during the manufacturing process. There are several possible explanations for this phenomenon. First, during the manufacture process many of the adsorptive sites of the activated carbon may become occupied by any of components of the foam matrix (e.g. surfactant, polymer, or cross linking agents). Data showing low surfactant recovery during the rinsing process supports this hypothesis. Second, during manufacture, PAC becomes part of the polyurethane matrix, and PAC completely surrounded by the polyurethane may be physically blocked from contact by the toluene.

Honeywell foam exhibited excellent results for all tests performed for the preliminary evaluation. The low head loss reduces the risk of medium clogging. Its low density and good toluene adsorption capacity are reasons why it was selected for a more detailed evaluation. Polyurethane foam formulations M and J, which used WESTVACO PAC, had good adsorption capacity, but their wet density was high in comparison with other formulations tested. The best Calgon PAC foam was foam formulation D which had relatively high sorption capacity and low head loss which at the same time exhibiting low head loss and acceptable physical characteristics. For these reasons, it was also selected for the more detailed evaluation.

From the more detailed evaluation, it was found that in all cases, Honeywell foam absorption for the four compounds tested as single component solution presented Freundlich isotherm R^2 values greater then 0.9 indicating that the Freundlich isotherm adequately describes the experimental data. Also, a comparison of Freundlich parameters

revealed that p-xylene has a higher affinity for the media than does toluene, MEK, or MIBK. Aromatic compounds presented a higher adsorptive affinity than did ketones. Based on the Freundlich parameters, toluene presented better adsorption affinity for foam Formulation D than did MEK. In both cases, the K_f values obtained for foam Formulation D were more than an order of magnitude smaller than those found for Honeywell foam.

For adsorption of multicomponent solution to Honeywell foam in batch tests, a comparison of Freundlich parameters reveal that p-xylene had a higher affinity for the media than did other compounds. The slopes of the line changed for all compounds tested indicating competitive adsorption.

BDST analysis for columns containing Honeywell foam packing media indicated that Honeywell foam can be used to sorb contaminants as needed for sequencing batch operation of biofilters treating gas-phase contaminants. For example a column 192 cm in length could be loaded with toluene contaminated air for nearly 16.5 hr with a influent concentration of 500 ppm_v and a gas surface loading rate of 28.45 m^3/m^2*hr before more that 10% contaminant breakthrough occurred. In biofilter operation, some contaminants removal by biodegradation (instead of only abiotic sorption) is expected to occur during the FEED period, so it is likely that the duration of the feed period could be appreciably longer than the 16.5 hr in the example above.

Foam formulation D presented a different adsorptive behavior than did Honeywell when it was tested for BDST. The initial breakthrough was faster than that observed for experiments using Honeywell foam, and the height of the absorption zone was greater. This indicates that the Honeywell foam has more favorable adsorption kinetics than foam formulation D because the former foam had a shorter adsorption zone height and would thus require a smaller bed depth in order to achieve a specified removal efficiency.

Because competitive adsorption was observed to take place with multicomponent solutions, BDST analysis for a single compound cannot be used to predict design parameters for treatment of mixtures. In order to use BDST to predict the performance of multicomponent flows, a complete breakthrough for the specific mixture of the compound must be done, and from that test BDST can be determined and used for design purpose.

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APPENDIX 1

The relationship between surfactant concentration and soluble TOC was experimentally determined by measuring the TOC concentration of various dilutions of surfactant solutions containing either Pluronic™ P-65 or Tween 80. The TOC analysis method was identical to that described in section 3.31. Results for Pluronic™ P-65 are shown in Figure A1.1, and results for Tween 80 are shown in Figure A1.2. For Pluronic™ P-65, the surfactant concentration was determinate to be 1.595 times the TOC concentration. The reciprocal of this value, the TOC equivalent of the surfactant, was calculated to be 0.627g C/g P-65. For Tween 80, the surfactant concentration was experimentally determined to be 1.560 times the TOC concentration, and the TOC equivalent of the surfactant was calculated to be 0.641g C/g Tween 80. These experimentally determined parameters were used to calculate the concentration of surfactant based on TOC measurements for foam rinsing experiments described in section 3.1.3 and 4.1.1.

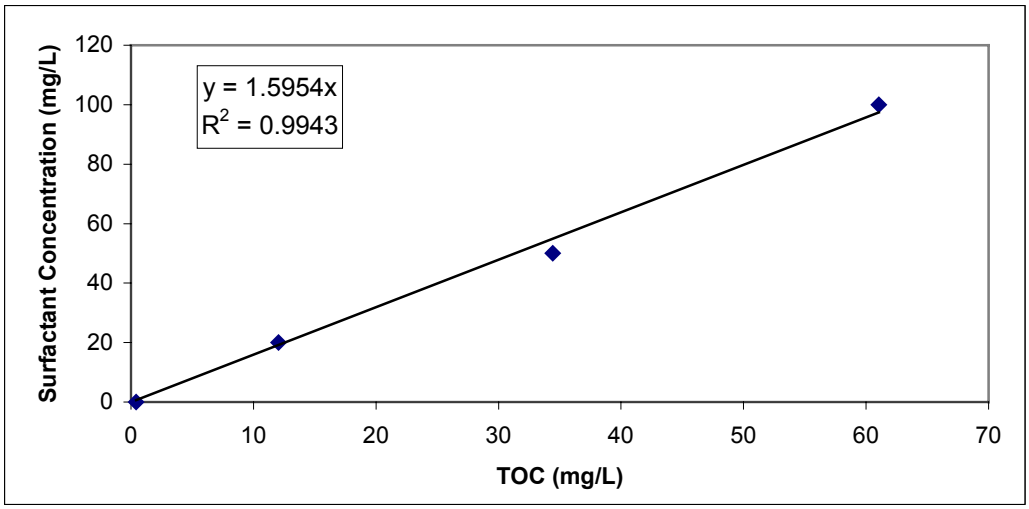

Figure A1.1: Calibration Curve for Pluronic™ P-65 surfactant solution and soluble TOC

Because the exact molecular formula of Pluronic™ P-65 is unknown (see Table 3.1), it is difficult to make a direct comparison between theoretical TOC equivalent for Pluronic™ P-65. Nevertheless, an assumption was made about of relative rate show of the molecular weight components. For this calculation, it was assumed that the value of X and Y variables shown in Table 3.1 were: X equal to 27 and Y equal to 23. Based on this assumption, the theoretical TOC equivalent is 0.547 g C/g P-65 (1.826 g P-65/G P-C). The value calculated based on this assumption is 10.2 % different from the experimentally determined value.

The molecular formula of Tween 80 is known (see table 3.1), and the theoretical TOC equivalent was calculated and compared to the experimentally determined value. The theoretical TOC equivalent for Tween 80 is 0.586 g C/g Tween 80. The calculated value based on the molecular formula is 8.3 % different from the experimentally determined value 0.641 g C/ g Tween 80

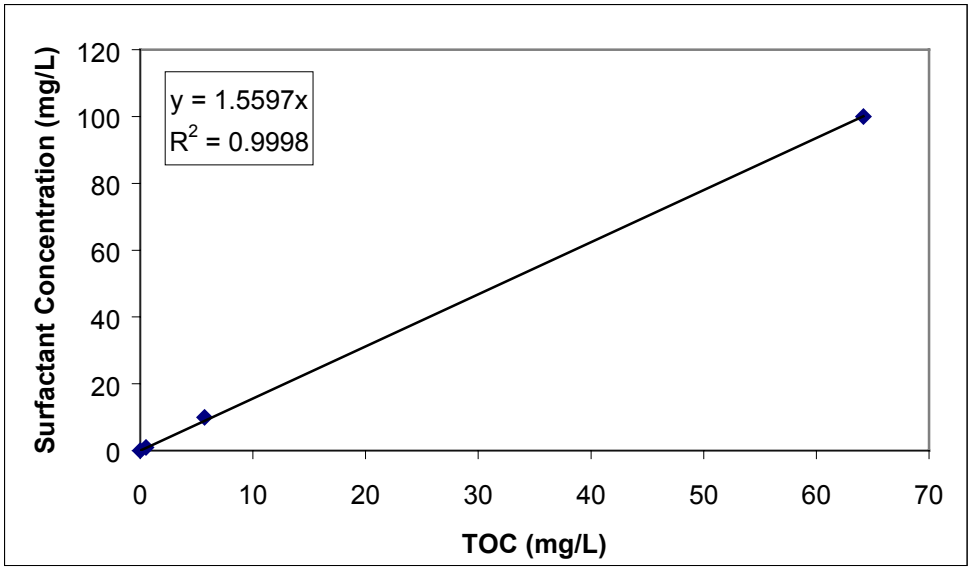

Figure A1.2: Relationship between Tween® 80 surfactant solution and soluble TOC

APPENDIX 2

CYLINDER No.	HYPOL					SURFACTANT + PAC MIXTURE					FOAM CYLINDER								RESULTS					FINAL % OF PAC INTO FOAM
	SPOON	CUP	SPOON + CUP	SPOON + CUP + DRY FOAM RESIDUE	DRY MASS FOAM RESIDUE	CUP	CUP + SURFACTANT	FILTER + TIN	FILTER + TIN + PAC	PAC	MOLD	MOLD + FOAM RESIDUE	DRY MASS FOAM RESIDUE	DRY FOAM CYLINDER (BEFORE WASHING)	MASS TOP AND BOTTOM CYLINDER	MASS CUT FOAM CYLINDER (BEFORE WASHING)	DRY MASS CUT FOAM CYLINDER (AFTER WASHING)	MASS OF FREE PAC IN THE FOAM	% OF FREE SURFACTANT	FINAL MASS PAC	MASS OF FREE SURFACTANT IN THE TOTAL FOAM	TOTAL MASS OF FOAM WITH SURFACTANT	MASS DRY FOAM SURFACTANT FREE	
1000 rpm and 30g PAC from Calgon																								
1	5.1	10.9	16.0	45.6	29.6	10.8	14.8	1.2	3.3	2.1	38.8	41.4	2.6	108.1	33.8	74.3	74.1		0.27%	27.9	0.4	140.3	139.9	**19.94%**
2	5.0	11.0	16.0	45.8	29.8	11.1	13.3	1.2	3.1	1.9	38.7	43.1	4.4	116.4	36.4	80.0	79.8		0.25%	28.1	0.4	150.6	150.3	**18.70%**
3	5.1	11.0	16.1	45.7	29.6	11.0	13.7	1.2	3.8	2.6	39.1	43.5	4.4	111.6	34.2	77.4	77.1		0.39%	27.4	0.6	145.6	145.0	**18.89%**
4	5.1	10.9	16.0	46.1	30.1	11.0	14.2	1.2	3.4	2.2	39.5	42.9	3.4	113.7	30.2	83.5	83.3		0.24%	27.8	0.4	147.2	146.8	**18.93%**
5	5.0	11.1	16.1	45.1	29.0	11.0	13.4	1.2	3.2	2.0	38.3	42.6	4.3	111.4	38.0	73.4	73.1		0.41%	28.0	0.6	144.7	144.1	**19.43%**
MEAN	**5.1**	**11.0**	**16.0**	**45.7**	**29.6**	**11.0**	**13.9**	**1.2**	**3.4**	**2.2**	**38.9**	**42.7**	**3.8**	**112.2**	**34.5**	**77.7**	**77.5**		**0.3**	**27.8**	**0.5**	**145.7**	**145.2**	**19.2**
1800 rpm and 30g PAC from Calgon																								
1	3.3	19.4	22.7	69.4	46.7	20.0	21.9	1.2	2.5	1.3	42.2	45.3	3.1	108.4	30.3	78.1	77.6		0.64%	28.7	1.0	158.2	157.2	**18.26%**
2	3.2	19.5	22.7	66.0	43.3	19.1	21.2	1.1	2.8	1.7	39.9	42.9	3.0	111.7	27.9	83.8	83.2		0.72%	28.3	1.1	158.0	156.9	**18.04%**
3	3.3	19.8	23.1	69.8	46.7	20.5	21.9	1.2	2.5	1.3	42.6	45.9	3.3	104.4	24.8	79.6	79.1		0.63%	28.7	1.0	154.4	153.4	**18.71%**
4	3.2	19.5	22.7	65.4	42.7	19.4	22.3	1.2	3.0	1.8	42.4	46.0	3.6	105.1	25.9	79.2	78.7		0.63%	28.2	1.0	151.4	150.4	**18.74%**
5	3.2	20.3	23.5	65.6	42.1	19.8	22.0	1.1	2.8	1.7	42.4	45.2	2.8	107.2	29.5	77.7	77.1		0.77%	28.3	1.2	152.1	150.9	**18.75%**
MEAN	**3.2**	**19.7**	**22.9**	**67.2**	**44.3**	**19.8**	**21.9**	**1.2**	**2.7**	**1.6**	**41.9**	**45.1**	**3.2**	**107.4**	**27.7**	**79.7**	**79.1**		**0.7**	**28.4**	**1.0**	**154.8**	**153.8**	**18.5**
1000 rpm and 75g PAC from Calgon																								
1	3.3	19.7	23.0	93.2	70.2	19.9	35.0	1.139	13.774	12.635	40.0	48.7	8.7	97.1	32.6	64.5	63.8	0.302	0.62%	62.1	1.1	176.0	174.9	**35.48%**
2	3.3	19.6	22.9	78.7	55.8	19.8	32.9	1.141	12.026	10.885	40.3	51.3	11.0	113.7	32.4	81.3	80.5	0.302	0.61%	63.8	1.1	180.5	179.4	**35.57%**
3	3.3	19.8	23.1	69.9	46.8	10.9	21.0	1.139	8.625	7.486	39.7	53.2	13.5	122.6	35.5	87.1	86.5	0.302	0.34%	67.2	0.6	182.9	182.3	**36.87%**
4	3.2	19.4	22.6	69.5	46.9	11.0	20.0	1.140	7.972	6.832	39.1	46.4	7.3	127.6	36.8	90.8	90.0	0.302	0.55%	67.9	1.0	181.8	180.8	**37.54%**
5	3.2	19.8	23.0	58.8	35.8	11.0	20.6	1.133	9.773	8.640	39.0	54.9	15.9	129.0	31.4	97.6	96.9	0.302	0.41%	66.1	0.7	180.7	180.0	**36.71%**
MEAN	**3.3**	**19.7**	**22.9**	**74.0**	**51.1**	**14.5**	**25.9**	**1.1**	**10.4**	**9.3**	**39.6**	**50.9**	**11.3**	**118.0**	**33.7**	**84.3**	**83.5**		**0.5**	**65.4**	**0.9**	**180.4**	**179.5**	**36.4**
1000 rpm and 0g PAC from Calgon																								
1	3.4	20.7	24.1	55.3	31.2	21.4					39.4	41.6	2.2	89.0	26.9	62.1	60.0		3.38%		4.1	122.4	118.3	
2	3.4	20.7	24.1	61.0	36.9	20.6					38.6	42.1	3.5	86.0	29.5	56.5	54.8		3.01%		3.8	126.4	122.6	
3	3.2	20.2	23.4	59.6	36.2	21.1					39.2	42.6	3.4	88.9	21.3	67.6	65.3		3.40%		4.4	128.5	124.1	
4	3.3	21.2	24.5	56.2	31.7	20.7					40.0	44.2	4.2	89.5	21.9	67.6	65.6		2.96%		3.7	125.4	121.7	
5	3.3	21.4	24.7	64.7	40.0	21.3					39.2	41.8	2.6	82.2	22.9	59.3	57.3		3.37%		4.2	124.8	120.6	
MEAN	**3.3**	**20.8**	**24.2**	**59.4**	**35.2**	**21.0**	**0.0**	**0.0**	**0.0**	**0.0**	**39.3**	**42.5**	**3.2**	**87.1**	**24.5**	**62.6**	**60.6**		**3.2**	**0.0**	**4.0**	**125.5**	**121.5**	**0.0**
1000 rpm and 45g PAC from Calgon																								
1	5.2	20.7	25.9	67.5	41.6	20.8	22.5	1.232	2.948	1.716	39.1	43.3	4.2	117.3	33.2	84.1	83.4	0.042	0.78%	43.2	1.3	163.1	161.8	**26.72%**
2	5.3	20.2	25.5	70.0	44.5	20.7	22.2	1.178	2.678	1.500	40.4	44.9	4.5	113.8	31.6	82.2	81.7	0.042	0.56%	43.5	0.9	162.8	161.9	**26.84%**
3	5.3	20.6	25.9	68.6	42.7	21.4	24.1	1.175	3.875	2.700	44.0	48.4	4.4	113.4	36.7	76.7	76.0	0.042	0.86%	42.3	1.4	160.5	159.1	**26.56%**
4	5.2	19.7	24.9	75.0	50.1	21.6	23.8	1.176	3.376	2.200	40.3	45.2	4.9	109.9	34.8	75.1	74.5	0.042	0.74%	42.8	1.2	164.9	163.7	**26.12%**
5	4.0	19.9	23.9	61.7	37.8	19.9	23.3	1.573	4.973	3.400	39.2	44.2	5.0	111.4	33.3	78.1	77.4	0.042	0.84%	41.6	1.3	154.2	152.9	**27.18%**
MEAN	**5.0**	**20.2**	**25.2**	**68.6**	**43.3**	**20.9**	**23.2**	**1.3**	**3.6**	**2.3**	**40.6**	**45.2**	**4.6**	**113.2**	**33.9**	**79.2**	**78.6**		**0.8**	**42.7**	**1.2**	**161.1**	**159.9**	**26.7**
1000 rpm and 15g PAC from Calgon																								
1	5.3	20.8	26.1	54.8	28.7	19.5	20.1	1.191	1.791	0.600	39.9	44.3	4.4	100.7	30.5	70.2	68.9	0.028	1.81%	14.4	2.4	133.8	131.4	**10.94%**
2	5.4	20.5	25.9	62.8	36.9	21.1	21.8	1.185	1.885	0.700	39.9	43.9	4.0	100.8	31.9	68.9	67.6	0.028	1.85%	14.3	2.6	141.7	139.1	**10.26%**
3	5.3	19.9	25.2	94.0	68.8	21.4	22.0	1.189	1.789	0.600	41.0	42.8	1.8	93.2	26.6	66.6	65.2	0.028	2.06%	14.4	3.4	163.8	160.4	**8.96%**
4	5.3	21.0	26.3	78.7	52.4	20.2	20.8	1.183	1.783	0.600	38.8	39.3	0.5	96.5	28.6	67.9	66.3	0.028	2.32%	14.4	3.5	149.4	145.9	**9.85%**
5	5.5	20.5	26.0	68.6	42.6	21.4	21.6	1.185	1.385	0.200	35.7	40.0	4.3	100.8	30.1	70.7	69.2	0.028	2.08%	14.8	3.1	147.7	144.6	**10.21%**
MEAN	**5.4**	**20.5**	**25.9**	**71.8**	**45.9**	**20.7**	**21.3**	**1.2**	**1.7**	**0.5**	**39.1**	**42.1**	**3.0**	**98.4**	**29.5**	**68.9**	**67.4**		**2.0**	**14.4**	**3.0**	**147.3**	**144.3**	**10.0**

CYLINDER No.	HYPOL					SURFACTANT + PAC MIXTURE			FOAM CYLINDER								RESULTS		FINAL % OF PAC INTO FOAM
	SPOON	CUP	SPOON + CUP	SPOON + CUP + DRY FOAM RESIDUE	DRY MASS FOAM RESIDUE	CUP	CUP + PAC	PAC	MOLD	MOLD + FOAM RESIDUE	DRY MASS FOAM RESIDUE	DRY FOAM CYLINDER (BEFORE WASHING)	MASS TOP AND BOTTOM CYLINDER	MASS CUT FOAM CYLINDER (BEFORE WASHING)	DRY MASS CUT FOAM CYLINDER (AFTER WASHING)	MASS OF FREE PAC IN THE FOAM	FINAL MASS PAC	TOTAL MASS OF FOAM WITH SURFACTANT	
45g PAC from Westvaco																			
1	5.661	11.720	17.381	56.222	38.841	10.958	12.577	1.619	34.072	46.997	12.925	115.878	28.811	87.067	87.067	0.042	43.381	167.644	**25.877**
2	5.884	77.932	83.816	44.870	-38.946	11.057	12.143	1.086	34.192	39.739	5.547	126.683	29.216	97.467	97.467	0.042	43.872	93.284	**47.031**
3	5.678	11.719	17.397	53.123	35.726	10.967	12.525	1.558	34.090	40.482	6.392	118.830	24.921	93.909	93.909	0.042	43.400	160.948	**26.965**
4	6.027	11.833	17.860	52.010	34.150	11.019	12.965	1.946	34.148	38.448	4.300	118.555	24.784	93.771	93.771	0.042	43.012	157.005	**27.395**
5	5.753	11.739	17.492	50.270	32.778	11.122	12.331	1.209	34.303	43.479	9.176	120.506	23.543	96.963	96.963	0.042	43.749	162.460	**26.929**
5	5.764	12.013	17.777	45.525	27.748	11.153	12.946	1.793	41.713	43.899	2.186	121.343	24.141	97.202	97.202	0.042	43.165	151.277	**28.534**
6	5.807	11.918	17.725	56.180	38.455	10.991	13.072	2.081	34.157	43.069	8.913	114.130	25.734	88.396	88.396	0.042	42.877	161.498	**26.550**
MEAN	**5.80**	**21.27**	**27.06**	**51.17**	**24.11**	**11.04**	**12.65**	**1.61**	**35.24**	**42.30**	**7.06**	**119.42**	**25.88**	**93.54**	**93.54**	**0.04**	**43.35**	**150.59**	**29.90**

APPENDIX 3

The mass of 5 different 600 mL glass-beakers was measured, and 45g of dry Westvaco PAC was poured into each one. The first three beakers were placed in a glass desicator with two petri dishes that contained 90 mL of toluene each. The other two beakers containing PAC were placed in a second desicator that contained two petri dishes that each contained 60 mL toluene. Every two hours the mass of each beaker was recorded and the PAC was stirred using a glass pipette. The experiment was continued until the mass of each beaker containing PAC was constant and no further weight gain occurred. A graph depicting weight increase versus time is provided in Figure A3.1. The difference between the initial and final mass of the beakers represented the total mass of toluene adsorbed.

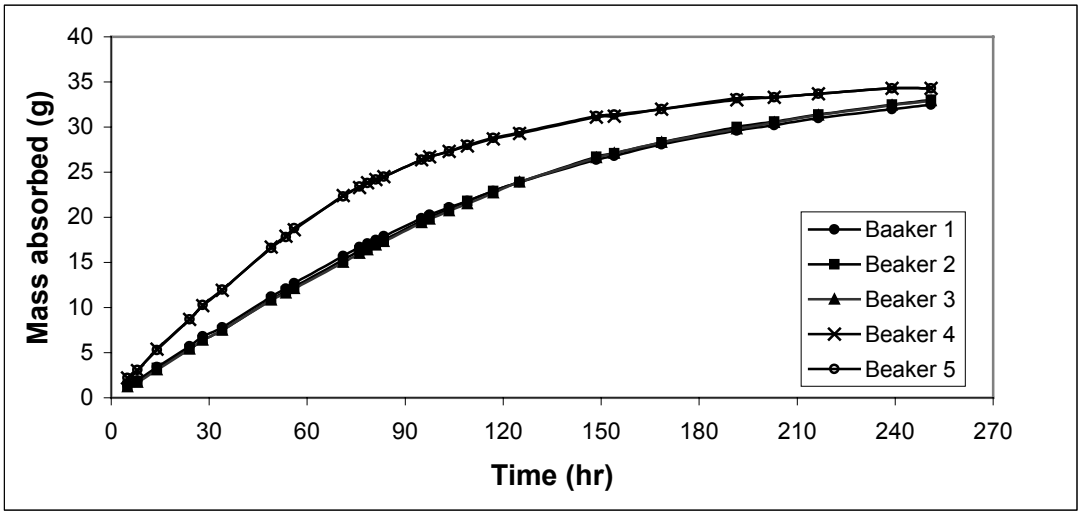

Figure A3.1: Adsorption of toluene by Westvaco carbon

APPENDIX 4

Figures A4.1, A4.2, and A4.3 present the adsorption data for foam formulation A at different influent concentrations and empty bed resident times (EBRTs).

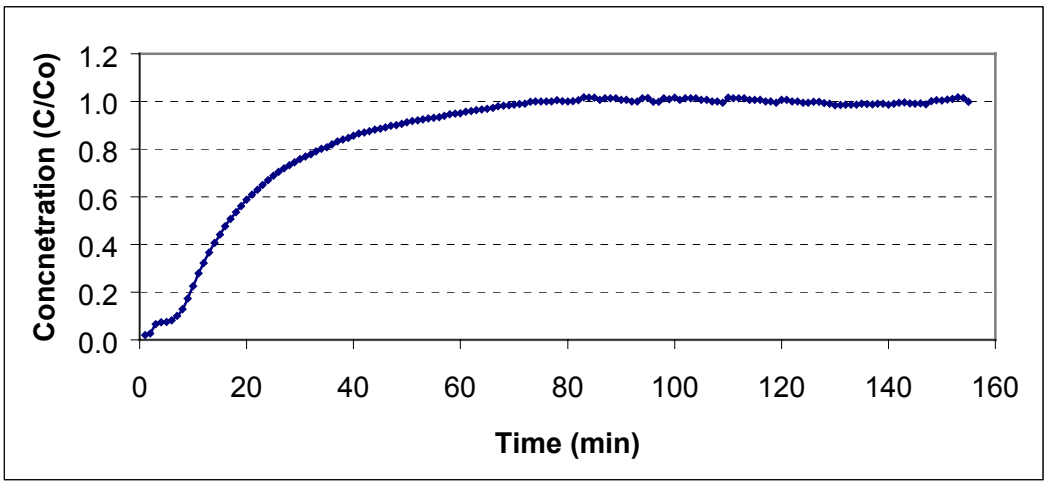

Figure A4.1: Adsorption of toluene by foam formulation A, 20 sec. EBRT, and 69.5 ppm_V gas concentration

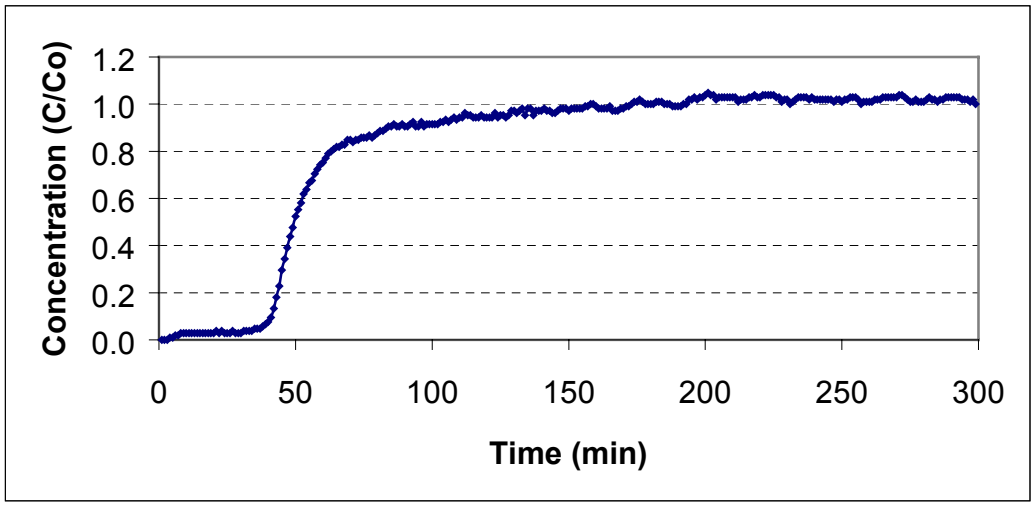

Figure A4.2: Adsorption of toluene by foam formulation A, 60 sec. EBRT, and 6.95 ppm_v gas concentration.

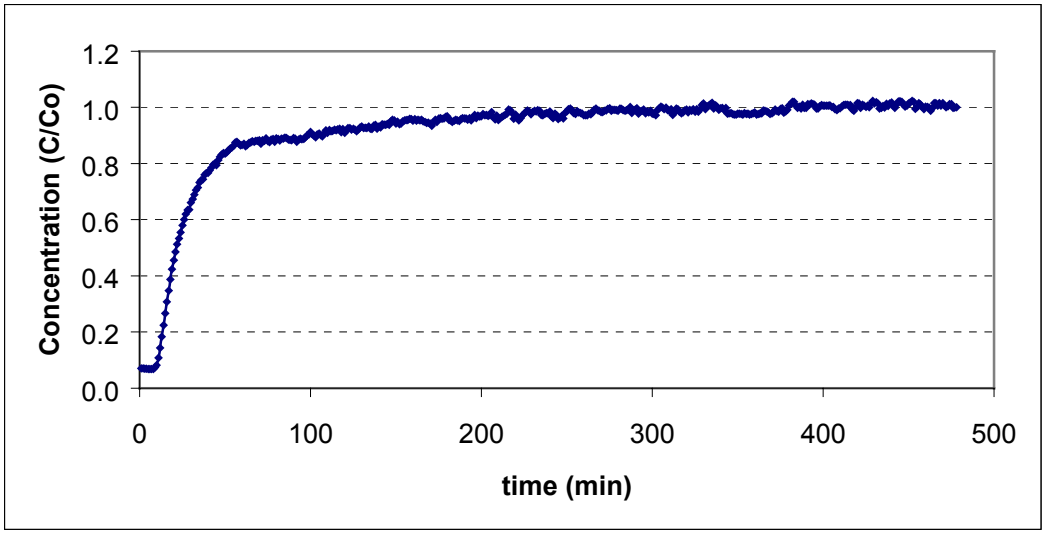

Figure A4.3: Adsorption of toluene by foam formulation A, 60 sec. EBRT, and 69.5 ppm_v gas concentration.

Figures A4.4, A4.5, and A4.6 present the desorption of toluene by foam formulation A.

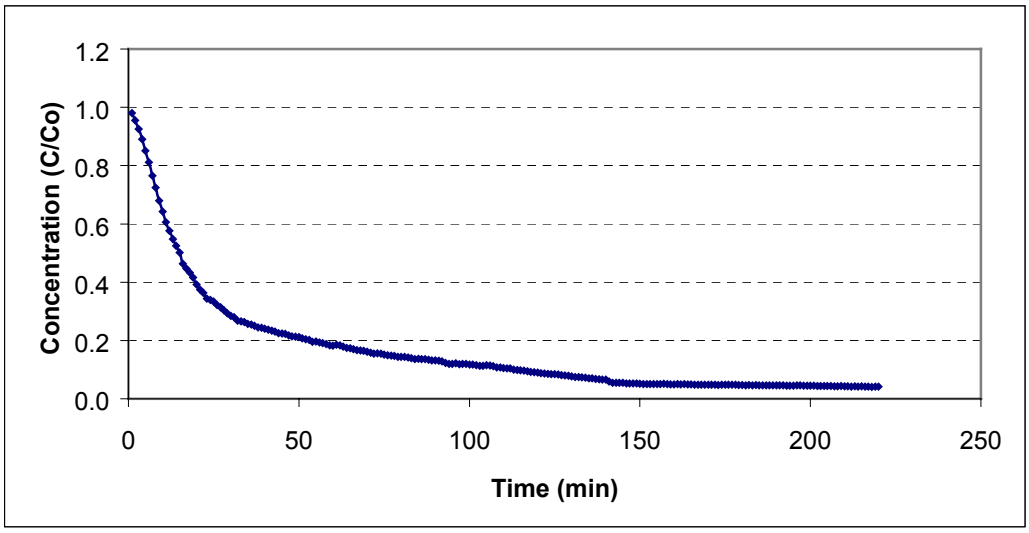

Figure A4.4: Desorption of toluene in foam formulation A, 20 sec. EBRT, and 69.5 ppm_v gas concentration.

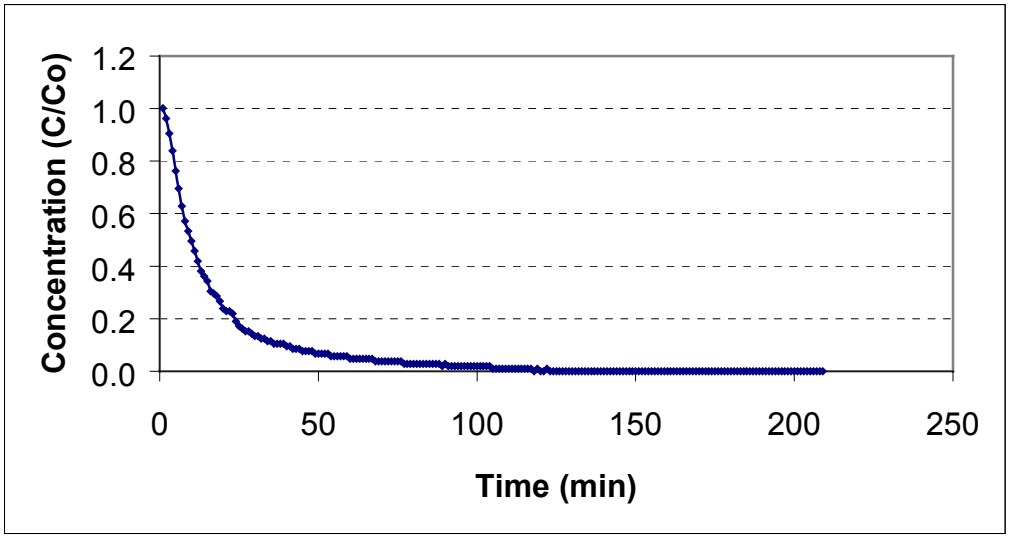

Figure A4.5: Desorption of toluene in foam formulation A, 60 sec. EBRT, and 6.95 ppm_v gas concentration.

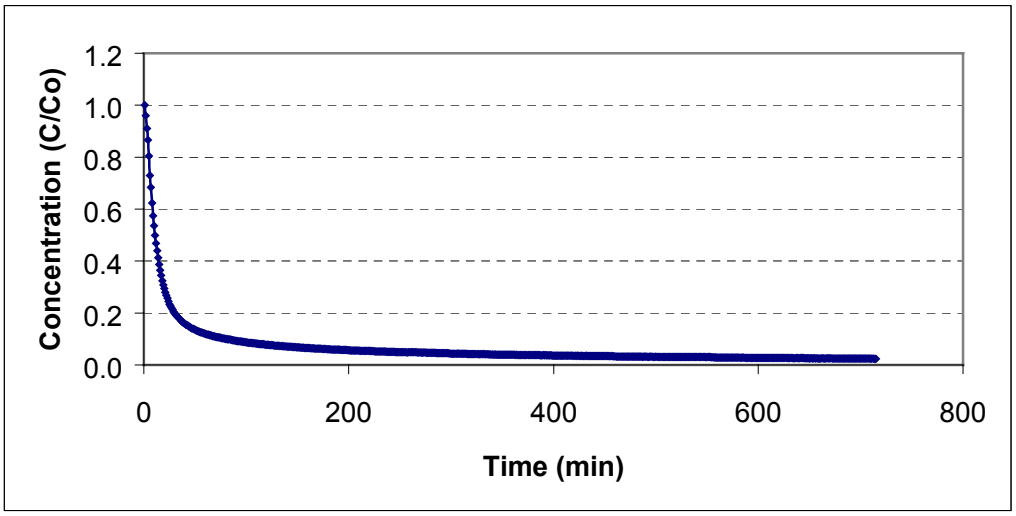

Figure A4.6: Desorption of toluene in foam formulation A, 60 sec. EBRT, and 6.95 ppm_v gas concentration.

Adsorption data for foam formulation D in a fixed-bed reactor at different influent concentrations and EBRT are present in the Figures A4.7, A4.8 and A4.9.

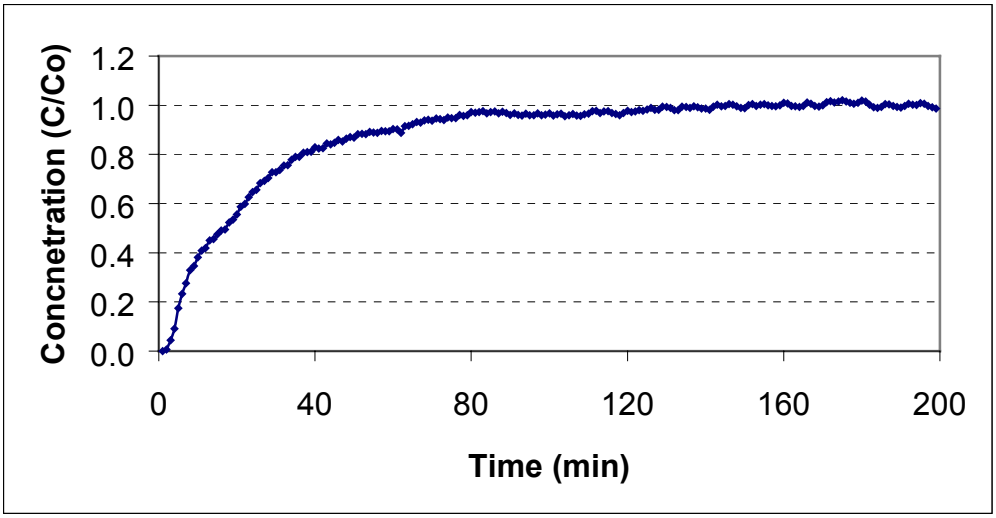

Figure A4.7: Adsorption of toluene by foam Formulation D 20 sec. EBRT and 69.9 ppm_v

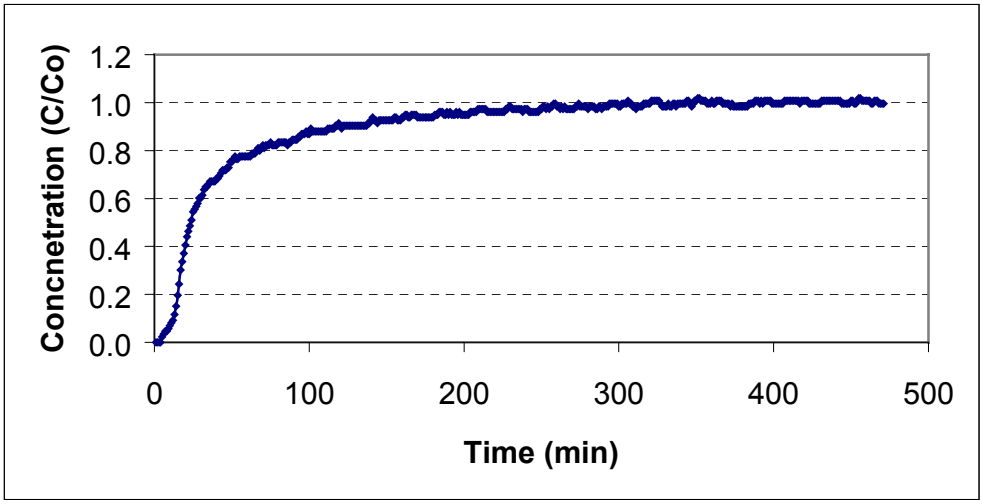

Figure A4.8: Adsorption of toluene by foam Formulation D 60 sec. EBRT and 6.95 ppm_v

Figures A4.10, A4.11, A4.12, and A4.13 present desorption of toluene for foam formulation D for 20 and 60 sec. EBRT.

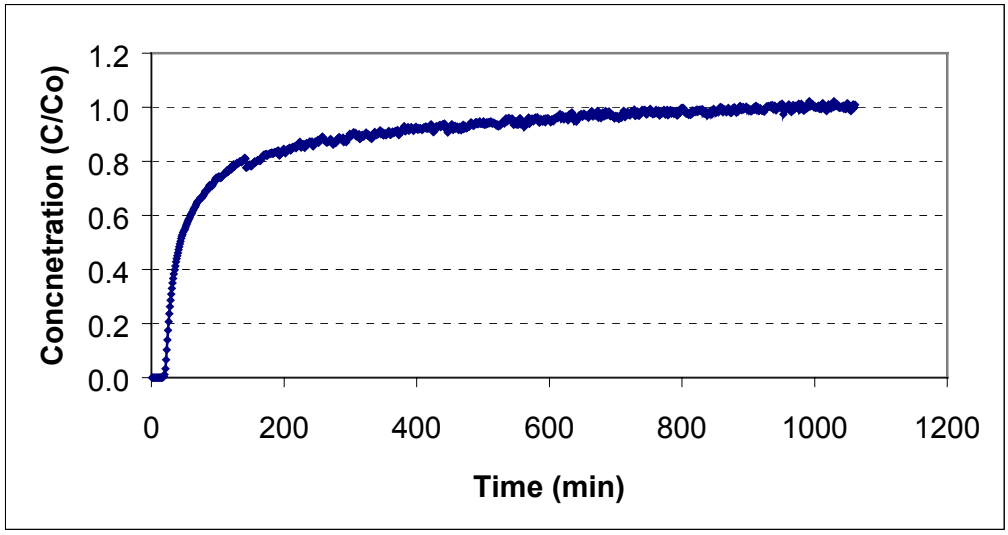

Figure A4.9: Adsorption of toluene by foam formulation D 60 sec. EBRT and 69.5 ppm_v

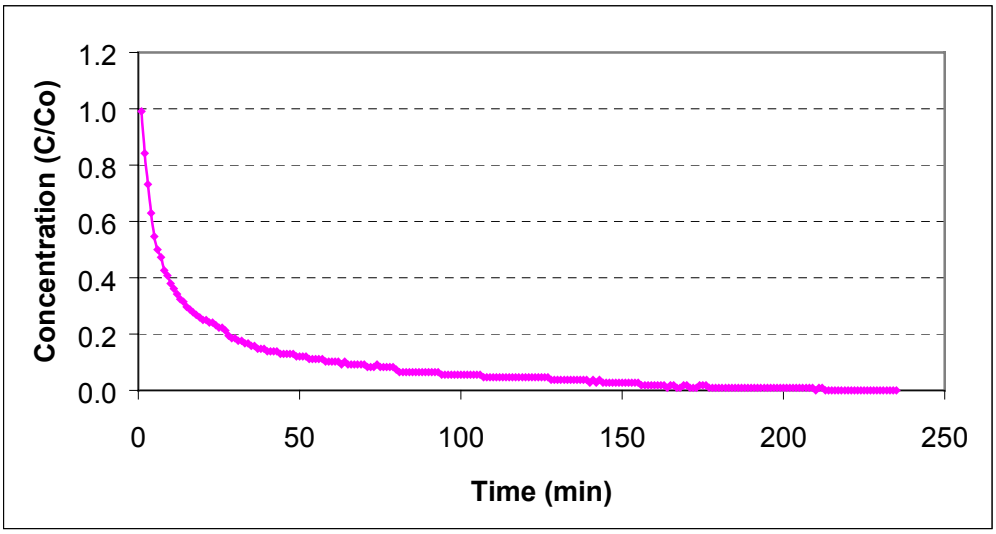

Figure A4.10: Desorption of toluene from foam formulation D 20 sec. EBRT and 6.95 ppm_v

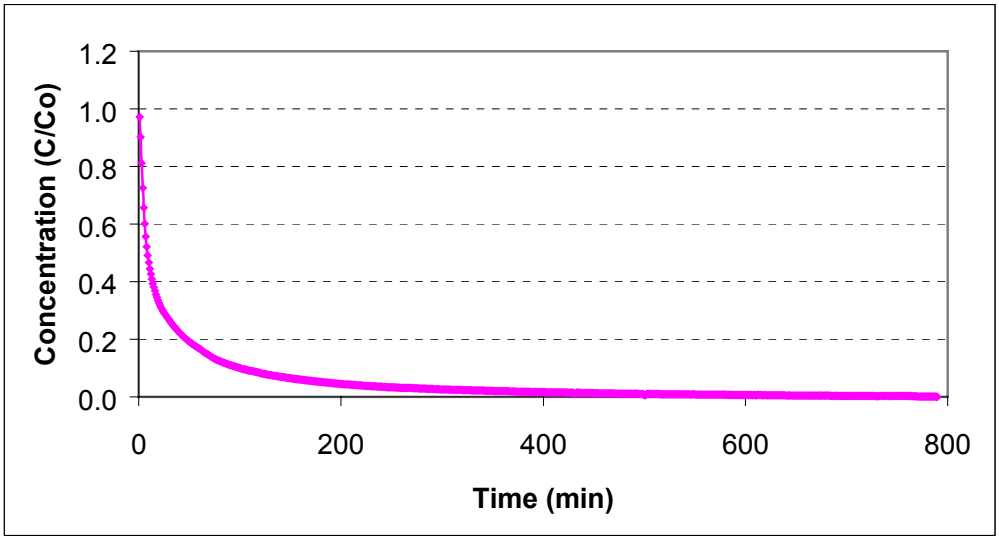

Figure A4.11: Desorption of toluene from foam Formulation D 20 sec. EBRT and 69.5 ppm_v

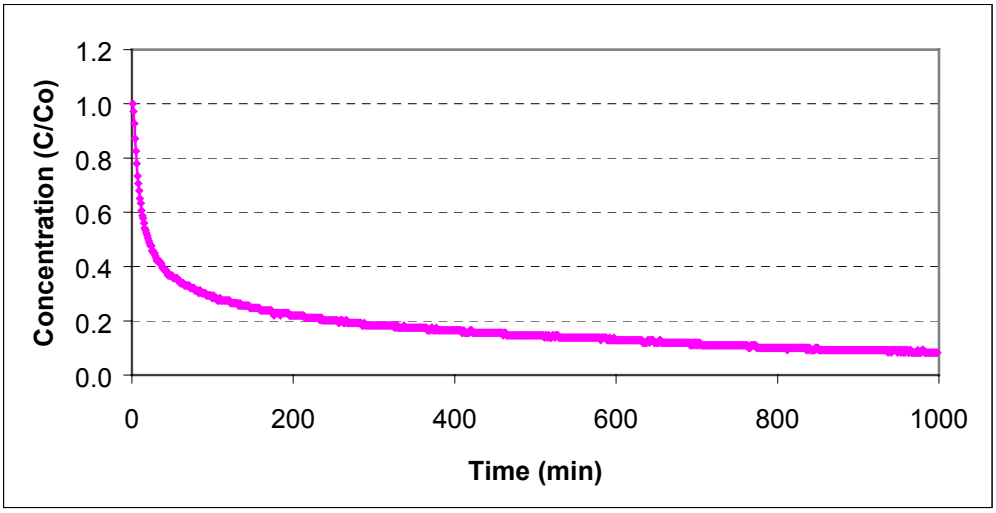

Figure A4.12: Desorption of toluene from foam Formulation D 60 sec. EBRT and 6.95 ppm_v

Desorption of toluene in foam formulation J with 20 second EBRT are shown in Figures A4.14 and A4.15.

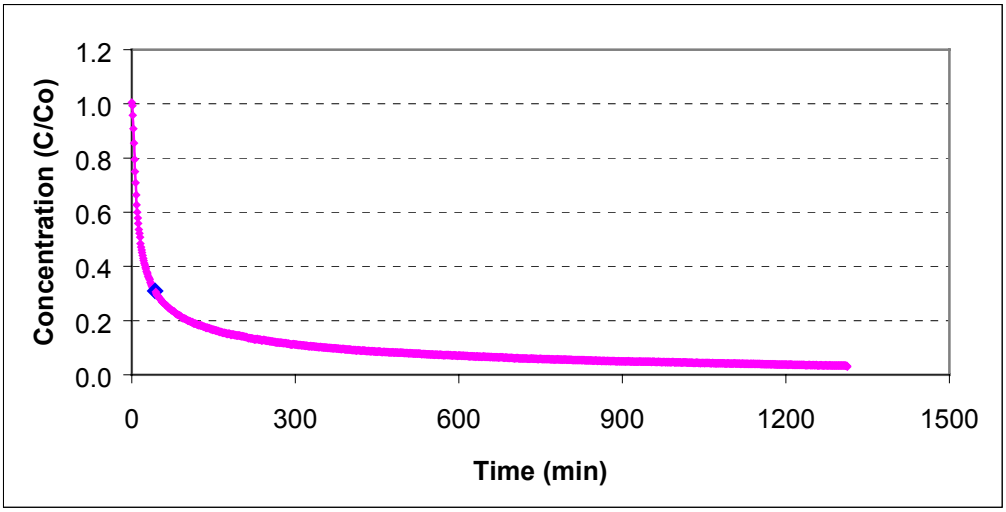

Figure A4.13: Desorption of toluene from foam formulation D 60 sec. EBRT and 69.5 ppm_v

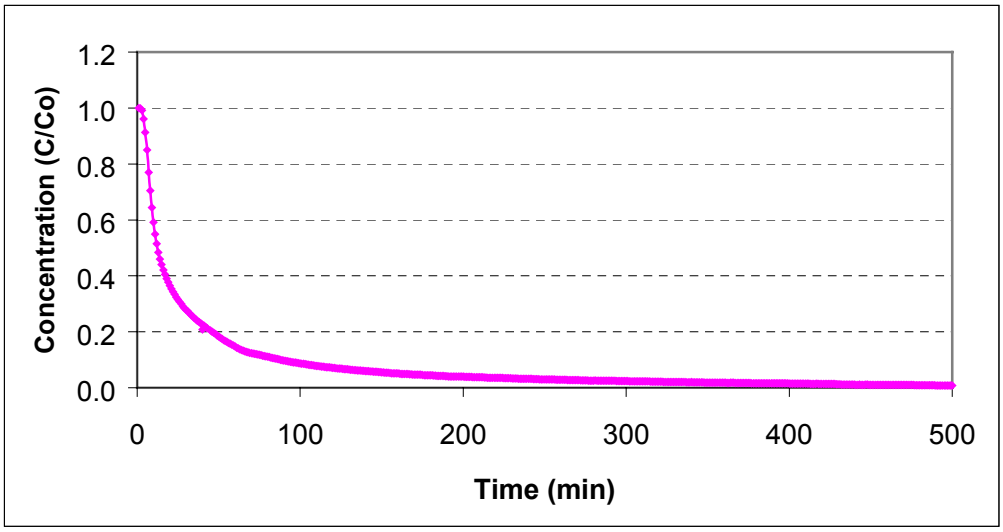

Figure A4.14: Desorption of toluene by foam Formulation J 20 sec. EBRT and 100 ppm_v

Fixed-bed adsorption data for foam formulation M at 6.95 and 99.86 ppm_v of toluene, and 20 seconds EBRT are shown in the Figures A4.16 and A4.17.

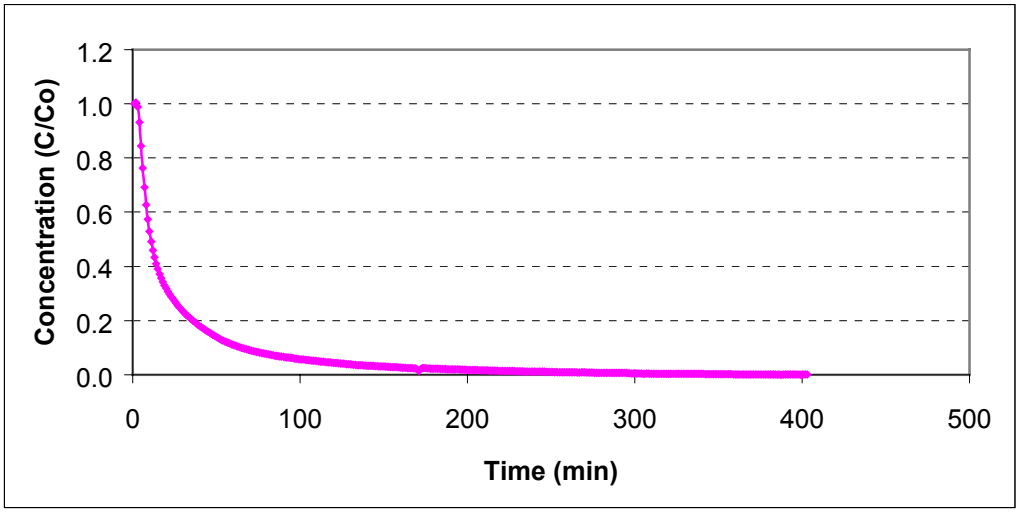

Figure A4.15: Desorption of toluene from foam formulation J, 20 sec. EBRT and 99.9 ppm_v

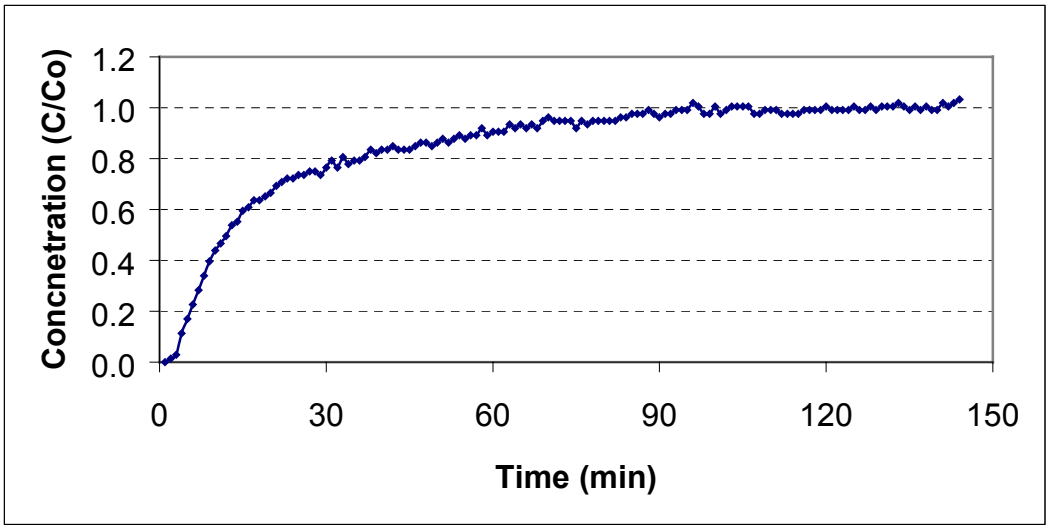

Figure A4.16: Adsorption of toluene by foam formulation M, 20 sec. EBRT and 6.95 ppm_v

Desorption data of toluene by foam formulation M is shown in Figures A4.18 and A4.19. The total desorbed mass was 27.54 mg, to 6.95 ppm_v and 20 sec. EBRT test, and 595.71 mg to 99.86 ppm_v and 20 sec. EBRT test.

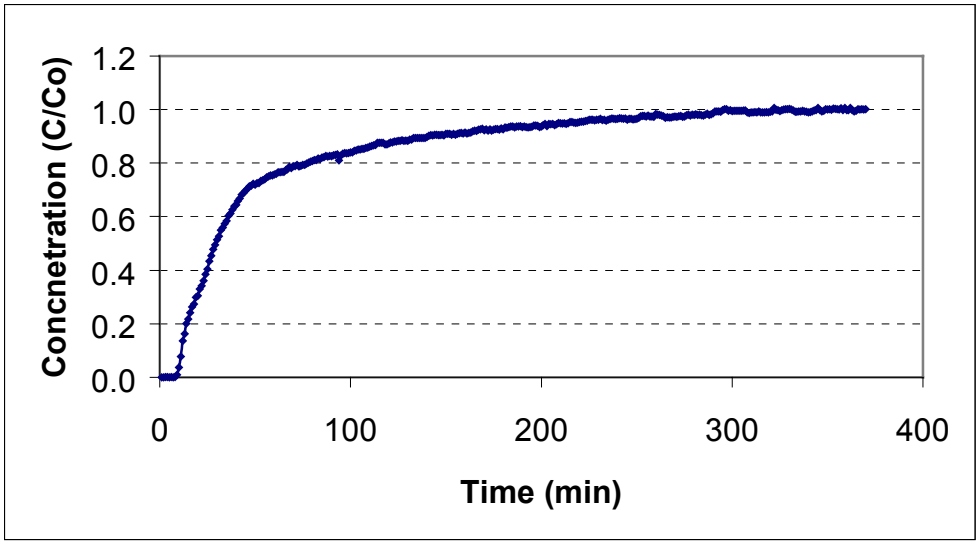

Figure A4.17: Desorption of toluene from foam formulation M, 20 sec. EBRT and 99.86 ppm_v

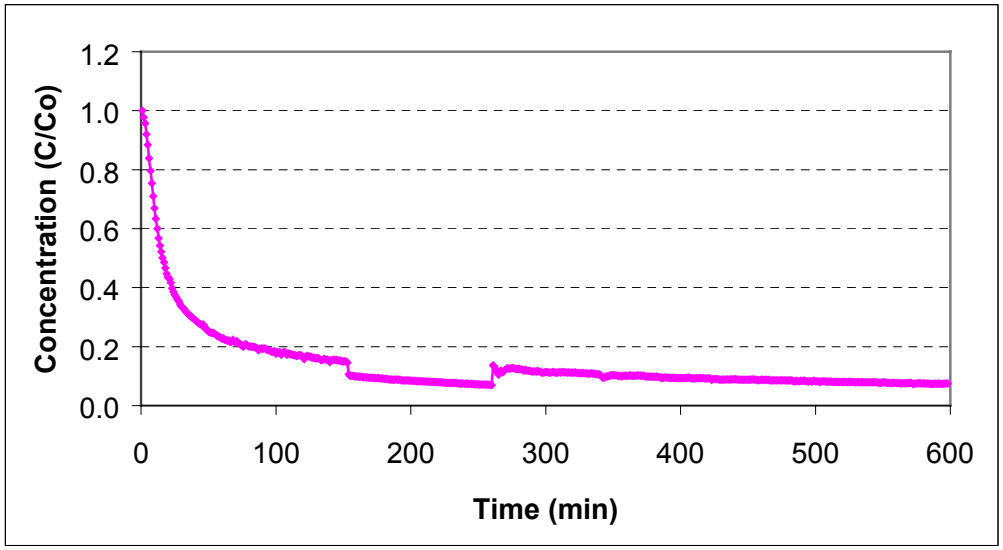

Figure A4.18: Desorption of Toluene from Foam Formulation M 20 sec. EBRT and 6.95 ppm_v

Figures A4.20, A4.21, and A4.22 show data collected from adsorption of toluene by Honeywell foam at 20 sec. EBRT.

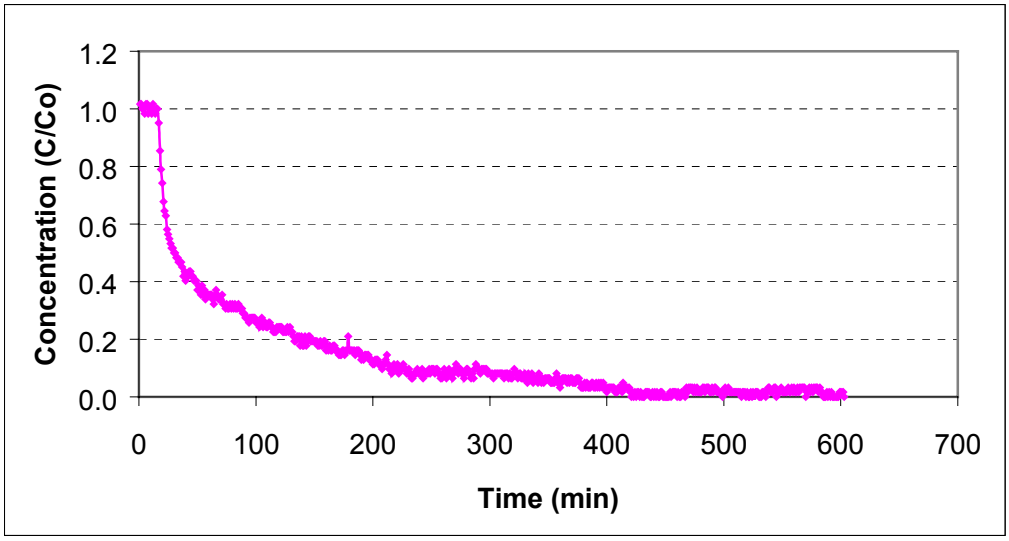

Figure A4.19: Desorption of Toluene from Foam Formulation M 20 sec. EBRT and 99.89 ppm_v

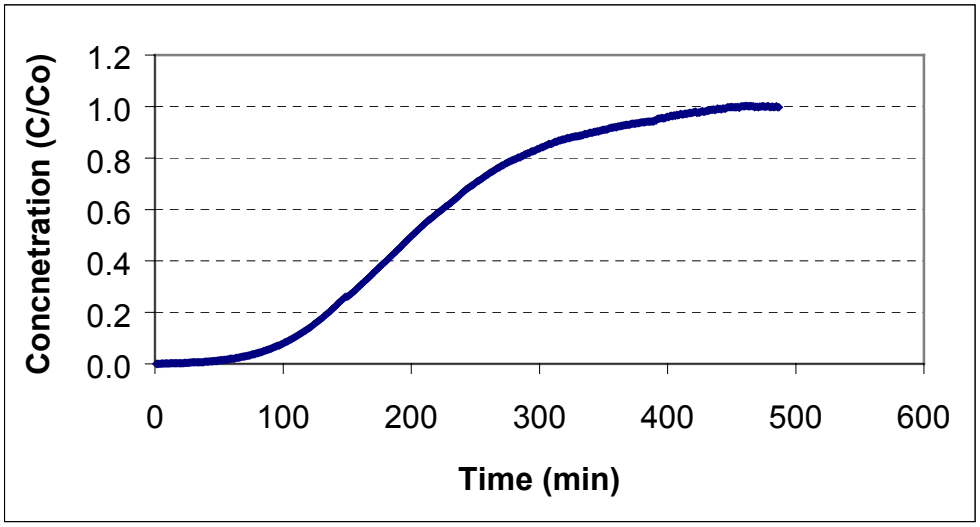

Figure A4.20: Adsorption of Toluene by Honeywell Foam 20 sec. EBRT and 100 ppm_v

Desorption tests were performed for Honeywell foam under conditions similar to those used in adsorption tests. Figure A4.23 and A4.24 present desorption data for Honeywell foam with 20 sec. EBRT.

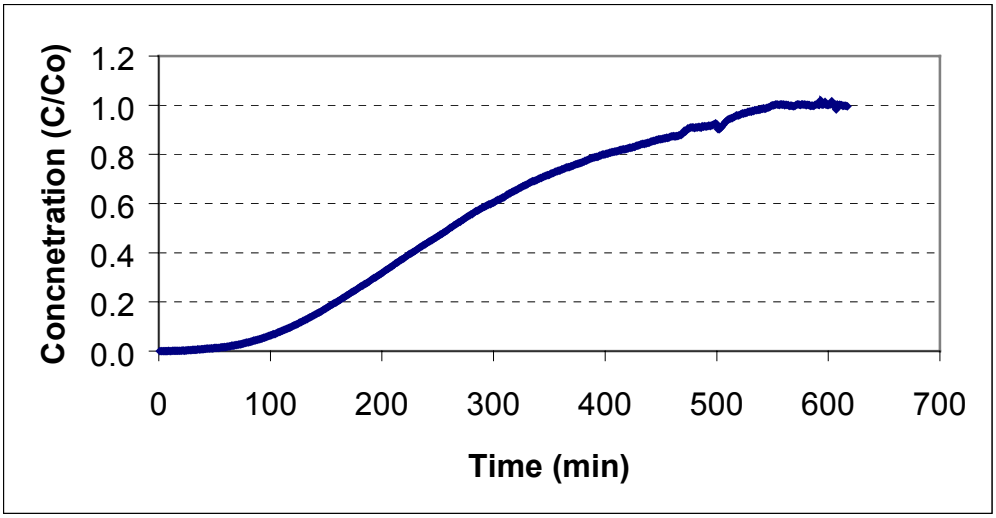

Figure A4.21: Adsorption of Toluene by Honeywell Foam 20 sec. EBRT and 100 ppm_v

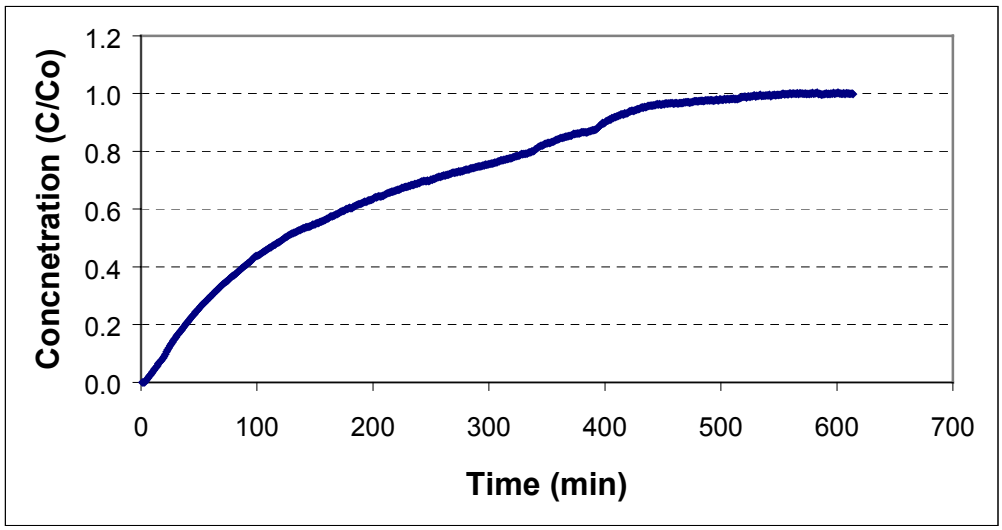

Figure A4.22: Adsorption of Toluene by Honeywell Foam 20 sec. EBRT and 500 ppm_v

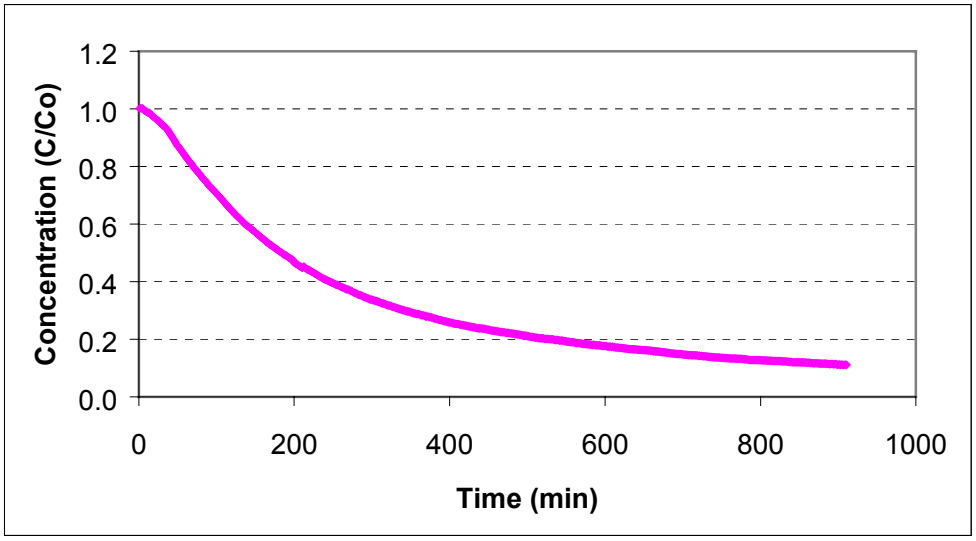

Figure A4.23: Desorption of toluene from Honeywell foam at 20 sec. and initial toluene concentration of 100 ppm_v

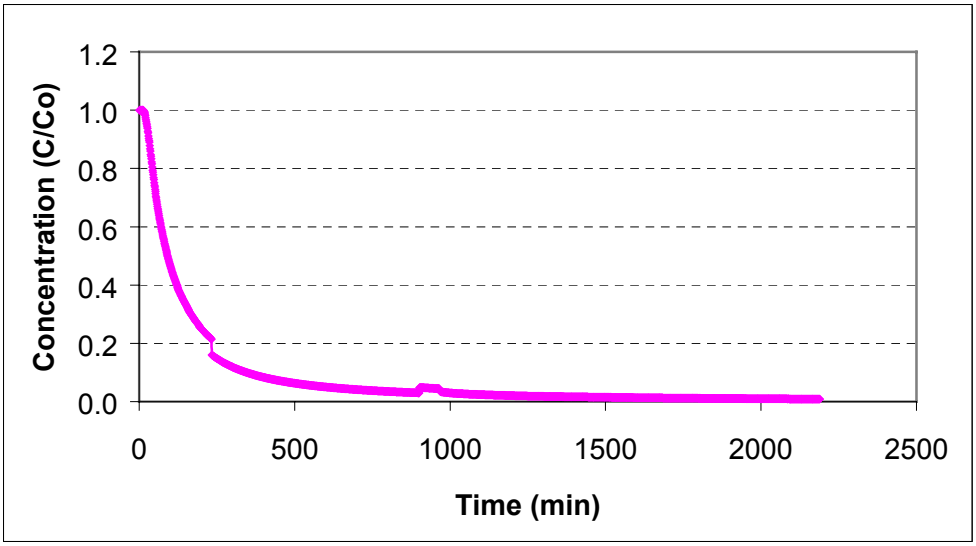

Figure A4.24: Desorption of toluene from Honeywell foam at 20 sec. and initial toluene concentration of 500 ppm_v

VITA

Felipe A. Martinez was born in Colombia, South America, in 1974. Felipe graduated from Universidad del Valle, Colombia, in 1996 with an honor Bachelor of Science in Civil engineering. Before completing his studies, Felipe worked for Constructora 81 and Conconcreto S.A. as engineer assistant. After graduation, he worked two years for City of Cali in the construction of the municipal wastewater treatment plant (PTAR). In 1998, he decided to continue with his education and move to Louisiana, USA, to learn English. One year later, during the fall of 1998, Felipe entered the graduate school of Louisiana State University, at Baton Rouge, LA, to obtain a Master of Science in Civil Engineering. He worked under the guidance of Dr. William M. Moe on media optimization for gas-phase biofilters. At present, Felipe is working for Hazen and Sawyer, P.C. at Boca Raton, Florida, as assistant engineer.